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# SULPHURI CONCENT

~~VEGETABLE~~ IN HEATED VESSELS

By P. PARRISH, A.I.C., M.I.CHEM.E.

AND F. C. SNELLING



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THE authors desire to  
Messrs. Charles Davison  
Tungay, of Messrs. Haughton's Patent Metallic  
Packing Co., Ltd., Messrs. The Lennox Foundry  
Co., Ltd., and The Thermal  
certain information afforded concerning their  
specialities, and for the loan of blocks.

P. PARRISH  
F. C. SNELLING.

*London,*  
*October, 1924.*



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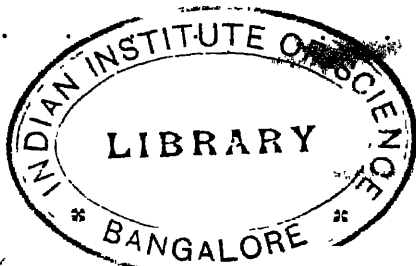
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# SULPHURIC ACID CONCENTRATION

## CHAPTER I

### INTRODUCTORY

THE concentration of sulphuric acid can be effected in plant which lends itself to a very sharp division into two classes, (1) that in which provision is made for the acid to be concentrated to come into contact with hot gases, and (2) that in which the acid to be concentrated is contained in heated vessels.

The first class of concentration plant is the subject of separate treatment (see "SULPHURIC ACID CONCENTRATION—By Hot Gases"). The second is the one which is dealt with in this book.

The earliest attempts to concentrate sulphuric acid to a high strength—say, 94–96 per cent.—were made in glass vessels of comparatively small size. The quality of the glass was not of the best, neither was the arrangement of furnace and brickwork in which these vessels were seated. Apart from the irregular heating throughout the period of concentration, the buildings in which the plants were disposed were not ideal. Draughts were not uncommon, and this factor, in combination with the crude method of heating the glass retorts, led to many breakages, with the inevitable

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loss of acid, and the evolution of an effluvium which was distinctly unpleasant.

Later, improved retorts were designed, and the type of setting was perfected. Even so, it was generally felt that there was a distinct need for a more foolproof plant, and recourse was had to stills

Platinum vessels had previously been used; indeed, the first still of this metal appears to have been tried early in the nineteenth century, but owing to porosity, leakages often occurred.

As progress in the metallurgy of platinum was made, more suitable vessels came to be used, but after a time, considerations of price, and the slow loss of this metal by the action of sulphuric acid, militated against the perpetuation of this type of plant.

Iron vessels were used in 1882, but owing to chemical action, which was tolerably serious with acids of concentrations below 92 per cent., they do not appear to have gained favour until Dreyfus improved upon the Clayton Aniline Company's British Patent No. 11544, of 1908, by the use of a recuperator tower.

An improved type of Dreyfus plant was used with a considerable measure of success during the war for emergency purposes. Many thousands of tons of acid slightly above 90 per cent. were brought to a strength of 96-97 per cent., but it is unlikely that the necessity for such plant will

## INTRODUCTORY

recur. Moreover, in any case, it would not be justified on economic grounds.

In this book it is proposed to trace the various stages of development to which brief attention has been directed, and to examine in some detail various types of cascade plants which have gained in popularity since the introduction of Vitreosil and the various silicon irons, and to attempt to forecast the future trend of development.

A chapter will be assigned to the materials of construction, particularly as affecting the types of plant with which this book deals, and some interesting particulars will be afforded concerning the transport and storage of concentrated sulphuric acid.

The general treatment of the various aspects is intended to be essentially practical, and such as will make an appeal to those who are interested either in the construction and working of such plants, or who are desirous of examining the economics of the subject.

## CHAPTER II

### MATERIALS OF CONSTRUCTION

IN the book on "Concentration of Sulphuric Acid by Hot Gases," a brief consideration is given to the more important materials employed in the construction of "hot gas" concentrators, and it is proposed, in this volume, to deal similarly with the materials used in plant for concentration in heated vessels.

#### IRON AND IRON ALLOYS

**Cast Iron.**—Cast iron cannot be described as a non-corrosive metal, but within certain limits it will withstand the action of concentrated sulphuric acid. This feature, together with its desirable and cheapness, makes it an important material for the construction of vitriol concentrators.

Castings for such purposes are usually specified as "chemical cast iron," and different foundries have a reputation for castings for definite purposes. Variations in the quality of the metal, however slight, are important, and much depends, also, upon the "finish" of the casting. The average composition of cast iron is as follows: graphitic carbon, 2 to 3 per cent.; combined carbon, 0.3 to 0.75 per cent.; manganese, 0.5 to 0.7 per cent.; silicon, 2 to 4 per cent., sulphur, up to 0.07 per cent.; phosphorus, 0.3 to 0.6 per cent. The important physical characteristics of the metal are approximately: density, 7 to 7.4; tensile



strength (tons per square inch), 9 to 10; melting point,  $1150^{\circ}$  C.; thermal conductivity C.G.S. units =  $0.199 (1 - 0.0029t)$ ; coefficient of expansion,  $1.16 \times 10^{-5}$ .

Cast iron is used for pots and dishes where the acid to be concentrated is not lower than 93 per cent.  $H_2SO_4$ . It will withstand cold sulphuric acid above 78 per cent strength. Hence, cast-iron pipes, eggs, etc., may be employed for acid above this strength.

**Wrought Iron.**—Wrought iron does not enter largely into the construction of concentration apparatus. It is much more readily attacked by weak sulphuric acid than is cast iron, but resists the action of acid above 80 per cent.  $H_2SO_4$ . Hence storage vessels and pipe lines for concentrated acid may be constructed of wrought iron if precautions are taken to exclude moisture.

**Semi-steel.**—The mechanical and physical properties of this metal vary with the method of its preparation; *i. e.*, the amount of steel or wrought iron added to the pig when casting. It has, however, a greater tensile strength than cast iron, and is better able to withstand sudden changes of temperature. Moreover, it is less liable to corrosion than wrought iron. Semi-steel may therefore be used advantageously for large castings, such as recuperator tower sections, etc.

**Silicon Irons.**—Although the introduction of "non-corrosive iron" is of comparatively recent

date, its development has been such that it is now extensively employed in almost all branches of the chemical industry. It is, however, particularly adapted to the construction of acid concentration apparatus.

Ferrosilicon alloys are marketed under the trade names of "~~IRON~~" "NARKI," and "TANTIRON" in England, and as "DURIRON" in America, while similar metals are manufactured on the continent as "ELIANITE" and "METTILURE." Matignon<sup>1</sup> has made a comprehensive study of the properties of these metals, and also gives an historical account of their development.

"TANTIRON" is made by the Lennox Foundry Co. at Glenville Grove, New Cross, London, S E. An average analysis of this material is :—

Silicon	14	to 16	per cent.
Total carbon	0.2	0.6	"
Manganese	0.25	0.35	"
Phosphorus	0.16	0.20	"
Sulphur	up to	0.05	"

It is hard and close grained, and has the appearance of white cast iron. Its mechanical and physical properties, compared for convenience with those of some other materials, are shown in the table on p. 19.

The allowance for contraction in casting is  $\frac{3}{16}$ -in. per foot, compared with  $\frac{3}{8}$ -in. for ordinary cast iron.

<sup>1</sup> *Chem. Ind.* (1919), 1283.

	Tant- iron.	Cast Iron.	Lead.	Regu- lus	Stone- ware.
Density . . .	6.8-7	7.3	11.3	10	2
Tensile strength .	6-7	9-10	—	—	—
Transverse strength (bars 12" x 1") .	1600 lb.	2500	—	—	—
Crushing strength (1-in cubes)	34 tons	40 tons	—	—	—
Transmission of heat . . .	215	230	115	80	20
Hardness . . .	35	24	1	2.2	32
Melting point, ° C	1200	1150	335	350	1800

"TANTIRON" is practically immune from corrosion by hot or cold sulphuric acid in all strengths. Results of tests in this connection show the percentage loss in weight of the metal after boiling in 98 per cent. sulphuric acid for 24, 48, and 72 hours to be 0.10, 0.02, and 0.02 respectively.

Although "TANTIRON," as originally produced, was incapable of being machined, a quality of this metal is now manufactured which may be drilled, turned, screwed, or planed. It is claimed that, in the attainment of this desirable property, none of the acid-resisting qualities of the material has been sacrificed. Large or small castings can be supplied in the shape of basins, pans, covers, coolers, eggs, pipes, etc., and where high tensile strength is desired, steel pipes, etc., may be lined with "TANTIRON."

"NARKI" metal is manufactured at the Waterloo Foundry, St Helens, by John Varley, Ltd. It is claimed that the mechanical properties of this material approximate to those of cast iron,

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and it is certain that it may be machined almost as easily as the latter metal. It is practically non-corrosive, and has been applied successfully to difficult situations. "NARKI" metal may be obtained as pipes, pans, beakers, coolers, recuperator towers, cascade basins, and other various special parts for acid concentration plant.

"IRONAC" is a product of Haughton's Patent Metallic Packing Co., Ltd., of 30 St. Mary-at-Hill, London, E.C. This metal has been applied very extensively in the construction of all types of vitriol concentrators. It may be obtained in a variety of stock patterns and sizes of beakers, pipes, beakers, coolers, etc. Complete cascade concentrating plants of different types can also be procured.

**Copper and Copper Alloys.**—A copper alloy specially suitable for making cocks and pipes as well as bolts and nuts, etc., for use in conjunction with silicon iron apparatus, is manufactured by the Lennox Foundry Co. This metal has a tensile strength of about 16 tons per square inch, is easily machined, and, in addition, is resistant to corrosion by sulphuric acid.

### IMPORTANCE OF SOUND CASTINGS

The importance of sound castings for concentrating vessels cannot be over-estimated, and, for this reason, a brief consideration of the more common defects and their causes will be given.

Several causes may contribute to the production

of bad castings, and these may originate (1) in the design, (2) in the moulding, or (3) in the metal

When designing special parts to be cast in iron or ~~cast-iron~~ <sup>steel</sup> iron, certain important rules should be followed. These affect alike the durability and the price of the article.

(1) Large flat surfaces should be avoided, and the thickness should be kept as uniform as possible.

(2) Where inequalities in thickness are unavoidable, the change in section should be a gradual one.

(3) Sharp, square corners, whether internal or external, are a source of fracture, and they should always be avoided.

(4) All large flanges should be webbed, and slots provided, rather than bolt-holes. (The latter consideration has particular reference to silicon-iron.)

(5) Long, projecting pipes on large vessels should be avoided, and the design generally kept as simple as possible, so as to make moulding and coring comparatively easy.

Defects arising through faulty moulding are most frequently due to the presence of gas in the moulds or cores, the result of which is the formation of "blow-holes," or scabs.

"Blow-holes" occur in the interior of the casting, and cannot usually be detected from the outside.

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They may be caused by the use of very wet sand, or an imperfectly vented mould. Casting at too low a temperature, or with an excess of sulphur, also gives rise to the defect. The sudden failure of a pot or dish is often due to the presence of a large blow-hole beneath the skin of the casting. In such a case, and if the article is otherwise sound, the faulty patch may be drilled out and plugged. Large blow-holes can generally be discovered, however, by a hammer test.

A "scab" is an irregular excrescence caused by the erosion of a part of the mould. Violent evolution of gas in any part of the ~~metal~~ sand will break up the sand, which will then be washed away, and the resulting cavity filled with metal. The incorrect placing of risers and gates will also produce the same effect. A small scab on a large casting is not of itself a very serious defect, but the presence of large scabs means that the displaced sand is contained in the casting, which should therefore be rejected. An apparent scab is sometimes proved to be a cavity (resulting from the careless removal of a riser or fin) filled with iron cement.

"Honeycombing" is usually apparent on the surface of the casting. It consists of a number of small cavities in close proximity, and is generally due to dirty metal and inefficient skimming. Spongy, or honeycombed, castings should never be accepted, particularly when the article is a

vessel in which concentration of acid is to be effected.

#### CERAMIC MATERIALS

**Porcelain.**—This material is rarely employed for large-scale apparatus, chiefly on account of cost. It is, however, sometimes used for the "calottes" of the Kessler plant. Porcelain will withstand high temperatures, but will not resist sudden changes of temperature. Its coefficient of expansion is about 0.0000036.

**Ceratherm.**—This is a heat- and acid-proof material, made by Guthrie & Co., at Accrington. It is mechanically stronger than porcelain or stoneware, and will withstand violent changes of temperature. It has a high thermal conductivity, and a low coefficient of expansion, and hence is suitable for the construction of coolers and condensers, etc. "CERATHERM" finds special application in the calottes of the Kessler apparatus, and in the lining of Gaillard towers. It can also be obtained as basins and covers, pipes, pumps, etc.

**Fused Silica.**—The introduction of Vitreosil basins and dishes by the Thermal Syndicate, Ltd., of Wallsend-on-Tyne, in 1907, was one of the chief factors in the successful development of the cascade system of concentration. More recently, many improvements in the production of fused silica ware have been effected, and complete cascade plant, comprising basins, preheaters, and coolers, may now be obtained.

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An interesting account of the history of the fused silica industry is given by Paget,<sup>1</sup> in which the work of early experimenters is reviewed. The development of a commercial method of fusion by means of an electric arc, or resistance furnace, was begun at Wallsend in 1903, by the collaboration of Hutton with Bottomley and Paget (B.P. 10670, 1904).

The raw material used in the manufacture of Vitreosil is pure quartz sand, containing about 99.7 per cent.  $\text{SiO}_2$ . This is fused to a plastic mass in an electrical resistance furnace, the heating core of which consists of plates or rods of carbon or graphite. The fusion, in the form of a hollow cylinder, is withdrawn from the furnace, after removing the core, and drawn into tubes, or blown into moulds to produce the required shape. The change from crystalline quartz to amorphous silica begins at a temperature of  $1470^\circ \text{C}$ ., and the pasty condition in which the material is worked is reached at about  $1800^\circ \text{C}$ . In the material produced by the furnace, innumerable small bubbles of air are occluded, and these bubbles are spread into threads, or laminations, during the blowing or drawing processes, thus producing the characteristic grain and opacity of the finished product.

The melting point of Vitreosil is  $1750^\circ \text{C}$ ., and its softening point is about  $1400^\circ \text{C}$ . When main-

<sup>1</sup> *J. R. Soc. Arts*, April 1924, p. 323.



tained at high temperatures (above 1100° C.), the material has a tendency to de-vitrify, and thus becomes very brittle. One of the most valuable of the characteristics of Vitreosil is its extremely small expansion and contraction with variations of temperature, the coefficient of linear expansion being approximately  $54 \times 10^{-8}$ —the smallest of any known material. Articles made of this material will thus withstand the most sudden and violent changes of temperature. The specific gravity of non-transparent Vitreosil is 2.07, and its hardness approximates that of hard glass. It is impermeable to gases, with the exception (at high temperatures) of hydrogen. The heat of conductivity is approximately the same as that of glass, viz., 0.002 (C.G.S. units), while the specific heat is 0.202 at 100° C. and 0.290 at 1000° C. The material is entirely unattacked by any acids or mixtures of acids, except hydrofluoric acid and phosphoric acid, in which it begins to dissolve at about 300° C.

## CHAPTER III

### CONCENTRATION IN LEAD PANS

IN the first book—"Sulphuric Acid Concentration—(By Hot Gases)"—attention is directed to the most economical method of concentrating chamber acid of (say)  $115^{\circ}$  Tw. (66.5 per cent.  $\text{H}_2\text{SO}_4$ ) to  $146\text{--}148^{\circ}$  Tw. (78–80 per cent.  $\text{H}_2\text{SO}_4$ ), by utilising the Glover tower for this purpose, and taking advantage of the sensible heat of the burner gases.

#### ADVANTAGES OF CONCENTRATION IN A GLOVER TOWER

The principal advantages which ~~this~~ method possesses over others are :—

- (1) The use of expensive fuel is dispensed with ;
- (2) Practically no labour is involved ;
- (3) The steam produced in the Glover tower is available for use in the chambers, and
- (4) There are no distillates of weak acid to handle, and hence no loss in this connection

#### DISADVANTAGE OF THE GLOVER TOWER

One disadvantage accompanying this method is due to the impurities which are introduced to the acid by reason of the burner gases containing dust, and, in some cases, arsenic and selenium. On this account, some works find it necessary to concentrate chamber acid in lead pans

#### THE PURPOSE FOR WHICH LEAD PANS ARE USED

In the heavy woollen district of Yorkshire there is a definite demand for sulphuric acid of about

80 per cent. strength, which is of a good, white colour, free from traces of nitrogen oxide and arsenic, and containing not more than 0.005 per cent. of iron. This quality of acid is known as "pan acid," and is used in the dye houses of the textile mills to a very large extent.

Here is an instance where lead pans have been used for many years with satisfactory results. Latterly, the cascade type of plant, with Vitreosil basins, has displaced lead pans in some works, but whether the newer method is more economical than the old one remains to be seen.

In this connection, it must be remembered that with an efficiently designed lead-pan system, heated with producer gases, six tons of lead, in the form of pans, will concentrate six thousand tons of acid to 80 per cent. strength before renewal is necessary, and thereafter, fully 90 per cent. of the original lead is recovered in the form of remelted pig lead.

With a fragile material of the character of Vitreosil, or the silicon irons, practically nothing can be realised for the broken parts.

Another point of importance in this connection is that any leakage which a lead pan develops reveals itself very early by the character and colour of the chimney gases, and it can be repaired readily without much expense. Not infrequently, with a fractured basin, acid is completely lost.

These are considerations which are apt to be

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ignored, when contrasting the two systems (*i.e.* lead pans *v.* Vitreosil or silicon iron cascade plants). Of course, it is appreciated that when rectified acid of 160–168° Tw. is required, lead is totally unsuitable, but the proposition is a different one when acid of only 80 per cent. strength is needed.

### DIFFERENT METHODS OF HEATING LEAD PANS

Concentration in lead pans may be conducted either intermittently or continuously, and the application of heat may be from above or below the lead pans. Moreover, waste heat may be used, or steam *via* coils may be applied, or advantage may be taken of the direct combustion of solid fuel, or producer gases.

Singularly few works now take advantage of the radiant heat of pyrites, spent oxide, or sulphur burners. It is far better and more economical to insulate the burners, and to utilise the heat for the concentration of additional quantities of acid in the Glover tower, than to go to the trouble and expense of erecting lead pans for extraneous concentration of acid. Moreover, where lead pans are so disposed, there is always a tendency for the acid to become discoloured, owing to the prevalence of oxide of iron dust.

There are few instances where the authors would be inclined to recommend the use of lead pans for acid concentration in conjunction with the burner plant. A few years ago, a somewhat ancient type

of acid plant was inspected at a superphosphate works, where the best use was apparently being made of the sensible heat of the burner gases.

The sulphuric acid plant in question merely comprised pyrites burners, potting oven, chambers, and Gay-Lussac towers. No Glover tower was provided. In order to operate the Gay-Lussac tower efficiently, chamber acid was concentrated in a continuously worked lead pan, so arranged that the hot burner gases served as the heating medium. The 80 per cent. acid produced in this way, after cooling, was blown to the Gay-Lussac tower, and used for the absorption of the nitrogen oxides. The nitrous acid was used for potting purposes.

Of course, it is not recommended that sulphuric acid installation should be erected without a Glover tower, but where old plants of the type in question exist, the arrangement outlined is undoubtedly a desirable one in the circumstances.

#### LEAD PANS HEATED BY STEAM COILS

The use of steam *vid* coils for acid concentration is not economical, and this method has long ago fallen into desuetude by reason of the expenses entailed.

#### INTERMITTENTLY OPERATED LEAD PANS

Batch concentration has now largely been superseded by continuously operated pans. The authors' introduction to an acid works more than a

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quarter of a century ago brought them in contact with a concentrating plant consisting of two lead pans, each of which was worked intermittently. Coke was used as the fuel, and a fire was placed at one end of the lead pan, which was supported on cast-iron rebated plates,  $1\frac{1}{2}$  ins. thick. A curtain arch protected the iron plates against the direct heat at the furnace end.

The pans in question were 30 ft. long by 5 ft. 10 ins. wide by 12 ins. deep, and they each produced 7 tons of acid per day. The B.O.V. was generally syphoned off in the afternoon, the chamber acid was subsequently fed to the pans, and the fire was restarted, concentration would then proceed throughout the next 18 to 20 hours. This method was not so destructive of the lead pans as the continuous one, where the first two or three pans suffered to a greater extent. The batch method of concentration involves the use of more fuel than the continuous one—usually about 15 per cent. based on the weight of the final acid.

### LEAD PANS HEATED FROM ABOVE

In the manufacture of bleaching powder by the Deacon's process, sulphuric acid is used for drying the chlorine and air prior to their passage to the preheaters and decomposers.

The cost of reconcentrating the acid used, which is diluted in the desiccating process, is an important consideration. But as the colour of the acid

is of no material consequence, and the production of 80 per cent. strength from the weak acid by the cheapest possible method is the desideratum, it was forced upon chemical engineers who were faced with this problem several years ago that concentration in lead pans heated from above constituted a satisfactory solution of the problem.

Lead-pan concentrators of the overheat type are

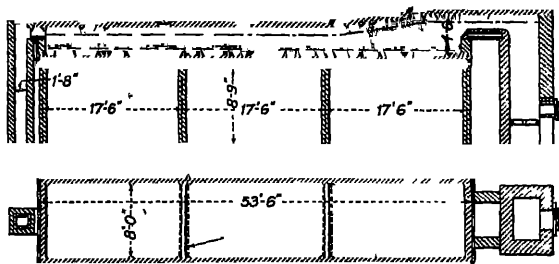


FIG. 1.—LEAD PAN CONCENTRATOR—OVERHEAT TYPE.

also used in some chemical factories for the concentration of arsenical sulphuric acid in the production of B.O V, where colour is of secondary importance, although in this connection it is important to consider the caution issued elsewhere in this book on the subject of concentration of arsenical chamber acid in lead pans.

Fig. 1 shows a typical concentration pan of the overheat type, used in connection with a plant for the production of chlorine in the manufacture of bleaching powder by the Deacon's process, where Hasenclever's modifications are adopted

## 32 SULPHURIC ACID CONCENTRATION

With the Hasenclever concentrator it is necessary to protect the lead-work with a lining of acid- and heat-resisting bricks. For the bottom it is usual to provide a 3-in. lining, but the sides are invariably 9 ins. thick, provided at the top with suitable skewbacks, in order that a camber arch constituting the cover can be sprung satisfactorily. In the centre of the camber arch, at regular centres, as shown, suitable openings for cleaning purposes are provided. These manholes are covered with tiles when the pan is in operation.

It will be appreciated that, owing to the character of the arch used as the cover, it is necessary to brace the sides of the pan securely at intervals of about 5 ft.

Near the furnace it is advisable to use an extra  $4\frac{1}{2}$ -in course, to the extent of about 10 or 12 ft., in order to give additional protection. It is at this point that the most stringent conditions are met. Not only is the temperature of the gas highest at this part of the concentrator, but the acid is also at its highest concentration.

Different kinds of acid-resisting cement have been employed for the joints of the brickwork, but the authors prefer the quick-setting mastic which is ( companion volume, dealing with "Sulphuric Acid Concentration by Hot Gases."

Dilute acid is fed to the pan at the end nearest the downcast flue and passes to the furnace end, where it is discharged through a special outlet



arrangement Thus the products of combustion travel in contrary direction to the flow of the acid. The pan shown in Fig. 1 is made of best Pattisonian refined chemical sheet lead, 24 lb. per square foot, a production of 200/250 tons of sulphuric acid per week, when dealing with dilute acid from the Deacon's plant of 108/110° Tw., and concentrating to a final strength of 140/144° Tw. This performance is equivalent to the use of 13.4 sq. ft. of pan surface per ton of B.O.V. produced per day.

#### WORKING OF THE OVERHEAT TYPE OF CONCENTRATOR

In starting a concentrator of this type, weak acid must be fed to the pan, and a constant depth maintained. A slow fire should be started, so as to dry the protecting brickwork of the pan and that of the downcast flue. Two or three days will be occupied in this operation, during which time the temperature of the acid will gradually be raised.

When the acid towards the furnace end has reached a temperature of about 160° C., a slow continuous feed of dilute acid can be commenced, and the fires increased. The supply of acid can gradually be increased in volume until the pan is yielding a quantity of acid approximating that of its rated capacity.

## 34 SULPHURIC ACID CONCENTRATION

It is advisable to control the strength of the acid by using a recording thermograph of the Cambridge and Paul type, placed at a point adjacent to the outlet end of the concentrator. The outlet should preferably consist of "Vitreosil" piping, set at an angle of about  $45^{\circ}$ , so that it discharges the hot, strong acid from the bottom of the pan.

The efficiency of the operation depends almost wholly on the care exercised in the firing. Usually, concentrators of this type are arranged with two fires. These should be cleaned alternately. The authors' experience leads them to prefer a mixture of coal and coke. The former gives a long flame, and the latter reduces the quantity of smoke and soot, which, apart from causing discoloration of the acid, also hastens the cleaning period.

It is more expedient to charge the fires often with a small quantity of fuel than to resort to heavy charging at infrequent intervals. The latter practice can only result in intense local heating, volatilisation of acid, a somewhat high escape, and the inevitable loss of acid.

The most satisfactory method of heating would be to use producer gas in suitable burners, using a secondary supply of heated air for the combustion. In this way soot could be avoided, and a uniform temperature maintained, with a certainty of increased life of the concentrator. Where producer gas or oil combustion is impossible, then strict supervision should be exercised and the

charging and cleaning of the fires should be carried out systematically.

With a properly controlled concentrator, the exit, when working to a single independent chimney, should not exceed the equivalent of 0.5 grain of  $\text{SO}_3$  per cubic foot.

Attempts to increase the evaporative efficiency of overheat lead pans by the employment of baffle walls, staggered and otherwise, have not been too successful. The adoption of such devices has led to an increased evaporation of something of the order of 0.7 lb. of water per lb. of fuel, but has occasioned trouble owing to the collection of soot and dirt, thus rendering cleaning more frequent.

#### CONTINUOUSLY OPERATED PANS HEATED FROM BELOW

Fig 2 represents a lead-pan concentration unit erected by one of the authors about twenty years ago, the special feature of which is that a gas producer is used

The pans constituting the unit in question are nine in number, three being built of 16 lb., three of 20 lb., and the remaining three of 24 lb. chemical sheet lead, each pan being 11 ft. 3 ins. by 5 ft. 9 ins. by 12 ins. deep. It will be seen that the brickwork is reduced to a minimum.

The lead pans are carried on cast-iron rebated

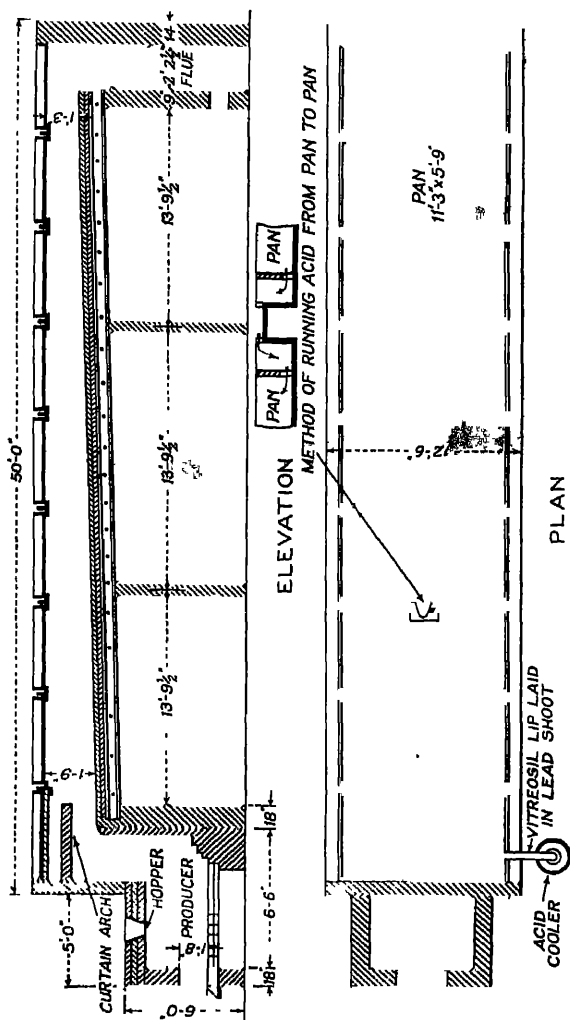


FIG. 2.—LEAD CONCENTRATION PANS—UNDERHEAT TYPE.

plates, about 2 ft. wide by  $1\frac{1}{8}$  ins. thick, which are supported in turn on cast-iron tee pieces placed at either end of each pan.

In order to ensure that the strongest acid passes from one pan to another, semi-circular pieces of lead are burnt to the end of each pan, where the overflow is arranged. These semi-circular pieces of lead, shown in section in Fig. 2, come within about 2 ins. of the bottom of the pan. Thus, all acid passing from one pan to another flows under the curtains in question. In this way, short-circuiting of the acid is avoided.

The producer is placed at the opposite end to that at which the chamber acid is introduced, so that a counter-flow is obtained. It is charged with coke each twenty-four hours, such coke having been allowed to dry on the top of the producer prior to being used. By employing a small quantity of steam continuously, it was found that the clinkering operation was not an onerous task, and could be effected in about half an hour. Invariably, 30 to 35 cwt. of coke were charged to the producer per day, and the concentration unit in question was capable of producing 20 to 22 tons of B.O.V. per day from chamber acid of  $106^{\circ}$  Tw.

When operating under normal conditions, the temperatures and specific gravities of the acid in the respective pans were invariably as follows.—

## 38 SULPHURIC ACID CONCENTRATION

Pan No.	Temp. ° F.	° Tw at 60° F.
1	154	106
2	184	110
3	218	116
4	240	122
5	270	132
6	298	134
7	320	143
8	343	145
9	330	148

The pans served for eight or nine months without necessitating any repair. After two years it was found advisable to renew the first three pans. The remaining pans, particularly the last three, operated satisfactorily for two or three years with-

consumption, representing on the average  $1\frac{1}{2}$  cwt. of coke per ton of B O V. (80 per cent.  $H_2SO_4$ ) produced, was a distinct saving on direct-fired, continuously operated lead-pan installations, but not so favourable as the results obtained later in a Gaillard tower, where 20 tons of B O V. from chamber acid of 106° Tw. could be obtained with a consumption of 17 cwt. of coke, representing 4.25 per cent. of fuel on the resulting B.O V, as contrasted with 7.73 per cent

Of course, with the Gaillard tower water-white B O V. could not be secured, but with the lead-pan installation an excellent quality of acid of almost perfect colour was obtained.

The labour entailed in working the concentrator

in question was very small, as it was attended to by the acid pumpers, who worked eight-hour shifts. For each ton of B.O.V. produced per day (24 hours) it will be seen that 27.7 sq. ft. of pan surface were required.

#### CONCENTRATION OF ARSENICAL CHAMBER ACID IN LEAD PANS

The authors have been face to face with the problem of concentrating acid in lead pans. Needless to say, their experience was a disastrous one, and it is important that a caution should be issued here and now against any attempt to concentrate acid of this quality in lead pans. What happens after a few hours, no matter how uniform may be the distribution of heat, is that the arsenical vitriol undergoing concentration becomes "milky" in appearance, and this is an incipient evidence that a leakage will sooner or later develop.

The "milky-pan" phenomenon is known to most acid manufacturers who have endeavoured to produce B.O.V. in lead pans from arsenical chamber acid. Arsenious acid does undoubtedly attack chemical sheet lead.

#### COST OF CONCENTRATING SULPHURIC ACID IN LEAD PANS

Prior to the war, the cost of concentrating chamber acid from 106° Tw to B.O.V. (80 per cent  $\text{H}_2\text{SO}_4$ ) in lead pans was of the following order:—

## 40 SULPHURIC ACID CONCENTRATION

	s.	d.
1.625 cwt of coke @ 12s 6d per ton . . .	1	0 2
Labour (say) . . .		6
Repairs . . .		4
Interest on capital, 5 per cent., and depreciation of concentration plant, 10 per cent Capital cost of installation £600. £90		
20 tons per day × 300 days = . . .		3 6
Cost of concentrating chamber acid to B O V . . .	2	1.8

From the above figures it will be possible, by modifying the items in respect of the price of coke, labour, and capital expenditure, to form a tolerably good indication of the costs of producing B.O.V. from chamber acid to-day.



## CHAPTER IV

### CONCENTRATION IN GLASS RETORTS

DURING the last fifty years large quantities of sulphuric acid have been concentrated in glass retorts. Even to-day, where crystal-clear rectified acid is required of exceptional purity, free from lead and iron, this method is in vogue. The methods formerly adopted for applying heat to glass retorts by the combustion of solid fuel were crude, and it is little wonder that fractures of the retorts occurred, with serious consequences in some cases to the rectifying men.

Briefly stated, the stages of development through which this method of concentration has passed have been the substitution of continuous working for intermittent operation, and the application of gaseous heating in lieu of the employment of solid fuel. More detailed references to these aspects will be made later.

Chance Bros, of Oldbury, near Birmingham, introduced the glass retort. These were made of a special thin flint glass, and blown as evenly as possible. Fig. 3 shows a sectional elevation of the glass retort in question, the method of seating, and the disposition of the furnace, etc.

It will be seen from this figure that the surplus gases leaving the glass retort setting are conducted under the lead concentration pans. In this way the consumption of fuel is very sensibly reduced. The retorts are approximately 2 ft. 8 ins. high from the bottom to the top of the neck, and 1 ft.

## 42 SULPHURIC ACID CONCENTRATION

10 ins. in diameter. They hold  $1\frac{1}{2}$  cwt. of acid, and weigh about 60 lb

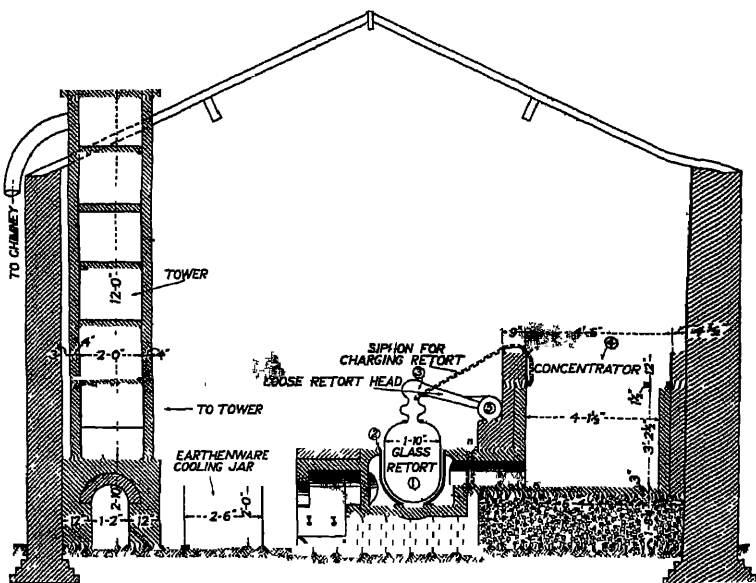


FIG. 3—SECTION OF PLANT FOR CONCENTRATING SULPHURIC ACID IN GLASS RETORTS.

Fig. 4 shows a slightly modified type of setting of a glass retort. Here the retort sits on a flat metal sand-bath, and protection from direct contact with the products of combustion is afforded by placing the fire at the side, and arranging for a protecting tile. A fume flue is provided to remove the acid vapours which are evolved during concentration. Any vapours condensed in their

passage through the flue are led to a collecting tank, and the uncondensed vapours are introduced to a condensation tower packed with suitable sized coke, where they are arrested by scrubbing.

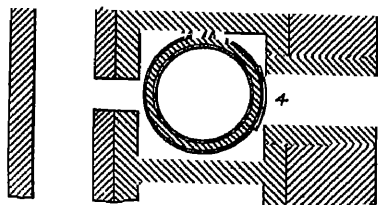
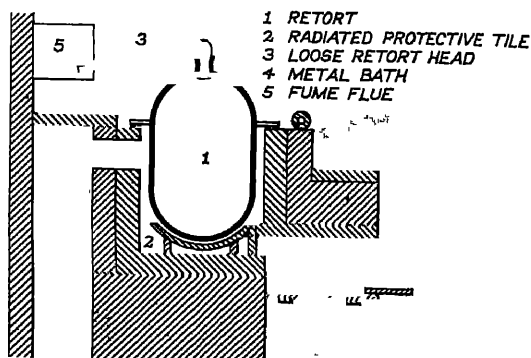


FIG. 4.—MODIFIED SETTING OF GLASS RETORT.

To aid the withdrawal of the vapours from the retort, and to obviate the use of any cement for the head of the retort, the condensation tower is coupled to the chimney shaft and sufficient suction is secured to prevent the escape of any vapours

## 44 SULPHURIC ACID CONCENTRATION

during concentration. The absence of a cement joint is a matter of importance, as the head has to be removed daily for emptying the rectified acid and for replenishing with pan acid.

Retorts are invariably assembled in groups, as shown in Fig. 5, and are disposed in close contiguity to the lead pans, from which a feed of hot acid is secured by means of a syphon.

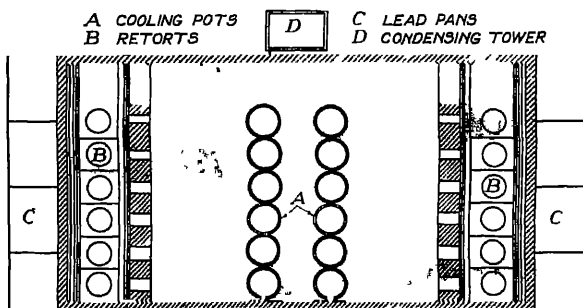


FIG. 5.—METHOD OF ASSEMBLING GLASS RETORTS IN UNITS.

It is usual to syphon the acid from the retorts, passing it through a suitable cooler before filling into carboys. In order to reduce loss through spillage to a minimum, it is advisable to pave the rectifying house with blue bricks, and to provide gutters and an inclined floor, so that any acid resulting from a cracked or broken retort can be collected.

A battery of retorts numbering from 12 to 40 is placed in a special building, so arranged that not

only can a constant temperature be maintained, but that there is freedom from draughts, which are a prolific cause of fractures. A retort house with 12 retorts should be capable of producing  $2\frac{1}{2}$  tons of R.O.V. per day.

The usual *modus operandi* is as follows: distillation proceeds during the day and is completed in the evening. During the night the acid cools partially. In the morning the retort heads are removed, and the acid is withdrawn by syphons consisting of capillary lead tubing. The acid is occasionally filled direct into carboys, but it is preferable to pass through coolers before filling into the requisite receptacles.

Working in 1909 with an installation of 24 retorts of the intermittent type, one of the authors secured the following results:—

January . . .	1075 carboys	50 tons of fuel.
February . . .	913 „	45 „ „

As has already been indicated, an improvement on that intermittent operation is to work continuously, according to the well-known Gridley method. In this system several retorts are placed in a stepped fashion with an inclined furnace. The retorts are connected by syphons. Fresh acid is fed to the top one, the acid in which, after being partially concentrated, gravitates to the adjacent stepped retort, and so on until the acid emerges at the cooler. A counter-current method of heating is adopted, the stronger acid coming into

contact with the hottest products of combustion, and the weak acid being preheated by the escaping gases.

One of the retorts of this improved system, as indeed the cascade arrangement itself, is shown in Fig. 6, which is largely self-explanatory. The retorts are set in sand in shallow iron pots. The acid is fed to the respective retorts through tubules attached to the retort.

At a continental works, where one of the authors erected a continuous plant, it was found that 45 tons of R.O.V. could be produced per week of 6 days with an installation of 16 retorts in four units, and the consumption of fuel per ton of acid concentrated from  $148^{\circ}$  Tw to  $166^{\circ}$  Tw. was 4 cwt. Two shifts of 12 hours, consisting of two men per shift, were employed.

A further improvement was subsequently introduced when gaseous heating was resorted to. It will be appreciated that this method is far preferable to the intermittent firing of solid fuel, with the accompanying introduction of spasmodic supplies of cold air.

Some manufacturers still repose implicit confidence in glass retorts where pure acid is required, but it is known that this method of concentration has been very largely replaced by the silica basin cascade system. It should be remarked that if breakages are to be avoided, the acid to be concentrated in glass retorts should be free from sediment

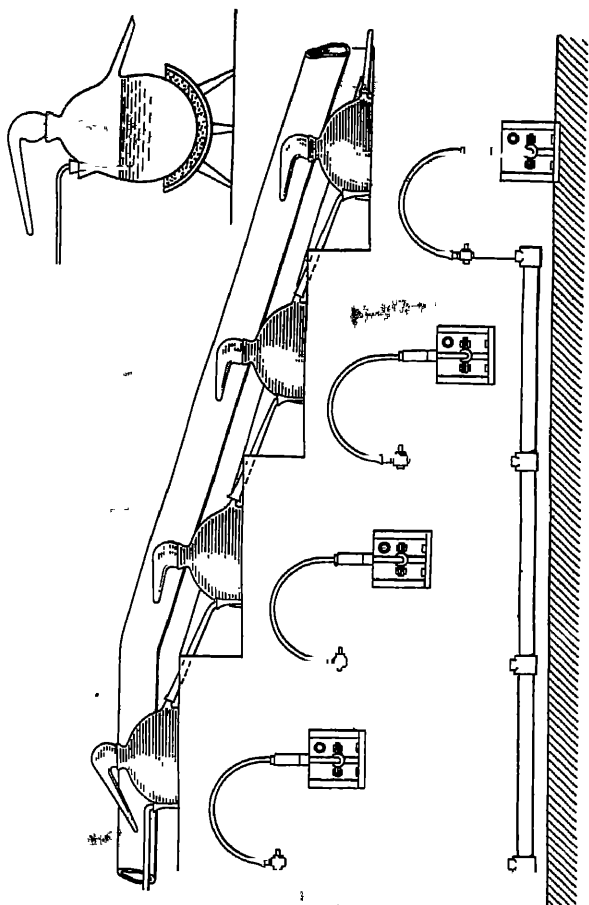


FIG. 6.—CONTINUOUS GLASS RETORT SYSTEM.

or dissolved impurities. Rarely is it possible to secure acid of a greater concentration than 93 to 94 per cent.  $\text{H}_2\text{SO}_4$  by this method.

## 48 SULPHURIC ACID CONCENTRATION

It will be interesting now to examine the costs of the concentration of sulphuric acid in glass retorts by the intermittent and continuous systems. It is necessary to remember that the installation costs are comparatively small, but that the fuel consumption is high, particularly with the intermittent method. Given an efficient type of glass-retort setting and careful working, neither depreciation of plant nor wear and tear will loom unduly large.

### COST OF CONCENTRATION IN GLASS RETORTS.

#### INTERMITTENT SYSTEM

	<i>s.</i>	<i>d.</i>
12 cwt. of fuel @ 1s. 6d. per cwt. . . . .	18	0
Wages (based on 12-hr. shifts) . . . . .	8	0
Breakages of retorts . . . . .	1	0
Repairs and maintenance . . . . .	1	6
Depreciation of plant and interest on capital . . . . .	2	6
	<hr/>	
Cost of concentrating one ton of acid from 115° Tw. to 166° Tw. . . . .	31	0

### COST OF CONCENTRATION IN GLASS RETORTS

#### BY THE CONTINUOUS METHOD

	<i>s.</i>	<i>d.</i>
6 cwt. of fuel @ 1s. 6d. per cwt. . . . .	9	0
Wages (based on 12-hr. shifts) . . . . .	6	3
Breakages of retorts . . . . .		9
Repairs and maintenance . . . . .	1	0
Depreciation of plant and interest on capital . . . . .	2	3
	<hr/>	
Cost of concentrating one ton of acid from 115° Tw. to 166° Tw. . . . .	19	3

It has been ascertained that the Chance stepped system of acid concentration has disappeared, but



there are still a few works concentrating sulphuric acid in glass retorts in single benches.

### PYREX GLASS

Pyrex is a borosilicate glass containing no metals of the magnesium-lime-zinc group, and no heavy metals. Its coefficient of linear expansion is 0.0000032 (less than half that of ordinary glass), and its softening point is about 600° C.

Pyrex was originally introduced as a material for laboratory and domestic apparatus, but has since been developed for the use of the chemical industry. Although little used in this country, it has been successfully applied in America to the construction of retorts, cascade basins, pipes, condensers, and tower fillings, and its use is rapidly spreading into many departments of the heavy chemical industry.

Acid concentration plants embodying the use of pyrex glass have been the subject of a paper by A. E. Marshall, before the American Institute of Chemical Engineers.

## CHAPTER V

### CONCENTRATION IN PLATINUM STILLs

THE concentration of sulphuric acid in platinum apparatus is now carried on only to a comparatively small extent, and generally, only when very pure acid is required.

Since the introduction of the platinum still in 1809, many modifications have been made, both in its design and the method of its construction, the old circular still being now very rarely employed. Modern all-platinum plant is made to the designs of Prentice or Delplace, each of whom makes use of shallow, rectangular pans.

Prentice's apparatus is shown in ~~Fig. 7~~, which is largely self-explanatory. For 5 tons of C.O.V. per day the dimensions of the still would need to be 3 ft by 1 ft 6 ins by 9 ins. The advantage claimed for this design is that, by reason of the corrugated bottom, the heating surface is increased by 60 per cent.

In the Delplace system, two stills, each 6 ft. by 1 ft. 6 ins., are employed. The first vessel is fed with acid of about  $144^{\circ}$  Tw., from lead pans, while the second still receives the partly concentrated acid produced by the first still. The vapours from both vessels are condensed in platinum tubes, the distillate from the second still being returned to the first, and that from the first still to the lead pans. The concentrated acid is first cooled in a cylindrical platinum cooler, and afterwards in lead coils.

Approximately 13 lb. of platinum would be used in a plant of this type (including condenser and

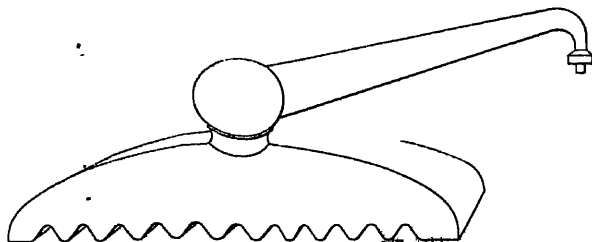


FIG. 7.—PRENTICE CORRUGATED PLATINUM STILL

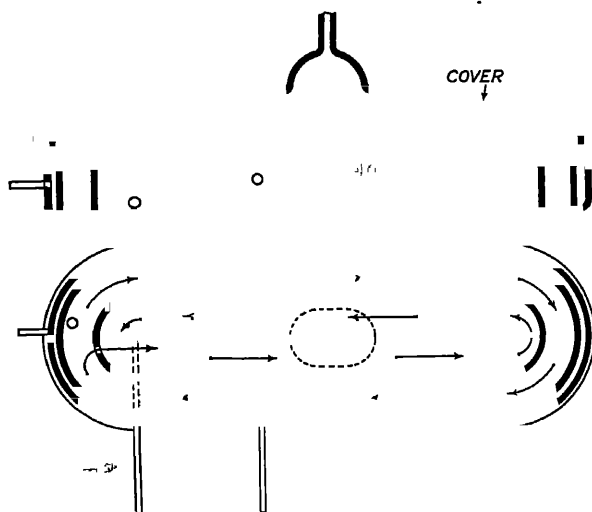


FIG. 8.—PLATINUM STILL AND COVER.

cooler) for each ton of 95 per cent. acid produced per 24 hours.

Fig. 8 illustrates a type of still made by F. Desmontes, Lemain et Cie. Two such stills may be used in the Delplace system. By forcing the acid to remain longer in the still, and incidentally by reducing the mixing of feed and concentrated acid, greater concentration, together with economy of fuel, is claimed. It is doubtful, however, whether the latter consideration is not outweighed by the greater initial cost of the plant and the increased depreciation due to a larger surface of metal being exposed to the acid.

#### PLATINUM PANS WITH LEAD COVERS

This type of concentrator was introduced as an attempt to produce a plant which retained the advantages of platinum, yet reduced its use to a minimum

In the Faure and Kessler system a shallow circular pan of platinum is covered by a lead hood built in the form of a water jacket. Such a still is shown in Fig. 9. The platinum dish, A, receives acid from lead pans through the pipe E. The vapours given off during boiling pass upwards through the cylindrical and conical covers, B and C, and leave the still by the outlet, H. Any condensate formed on the covers is caught by the lute formed on the rim of the pan at J, and is carried away by the pipe G. The concentrated acid leaves the pan by the overflow, F. The cooling-water inlet is shown at H, and the outlet

at O. Connection between the two sections forming the cover is made by a flanged joint at I. K and  $K_1$  are vents for air released from the cooling water during its passage through the jackets.

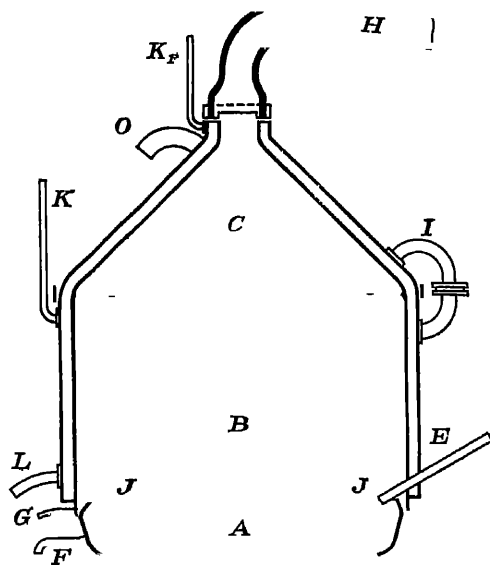


FIG. 9.—PLATINUM DISH WITH LEAD COVER.

Several <sup>1</sup> modifications of the original design of cover have been made. The Chemische Fabrik Rhenania <sup>1</sup> use a continuous coil of lead pipe, burning the walls in such a way as to form a gas-tight hood. In this case the cooling water

<sup>1</sup> Ger. Pat 64572

## 54 SULPHURIC ACID CONCENTRATION

enters at the bottom and circulates at a relatively high velocity. The size of the platinum dish depends upon the production required, about 75 oz. of platinum being used per ton of 95 per cent. acid produced per 24 hours. A dish weighing 45 lb., and measuring 3 ft 6 ins. diameter, would be capable of producing 7 tons of 95 per cent.  $\text{H}_2\text{SO}_4$  per diem.

Usually, two or more of these stills are arranged in cascade form, and follow a set of bottom-fired lead pans. The condensate from the covers and condensers is then returned to the feed.

### METHOD OF FIRING PLATINUM STILLs

By reason of the very shallow depth of acid (usually 2 to 3 ins.) with which modern stills are intended to operate, the method of firing is a matter of great importance. Very small heat variations will cause comparatively large fluctuations in the strength of the concentrated acid. It can readily be understood, therefore, that an ordinary intermittently charged coal fire will not give a temperature sufficiently steady for the regular production of concentrated acid from these stills. Mechanical stokers have been employed with good results, but gas firing (usually from a producer) is now almost invariably adopted as being the most regular and easily controlled method.

## QUALITY OF ACID AND FORMATION OF CRUSTS

Chamber acid contains varying quantities of iron salts (0.002 to 0.005 per cent), which separate during concentration as anhydrous ferric sulphate. This adheres to the bottom of the stills as "crusts," and necessitates frequent stoppages of the plant for cleaning. It is important that the crusts should not be allowed to grow, as otherwise they will become so hard that the ordinary method of cleaning, *i.e.*, washing with weak acid and water, will not remove them.

Glover acid is not suitable as a feed for platinum stills, owing to the large quantities of acid salts which it contains. Even where pure sulphur is burned, the Glover acid is contaminated by contact with the packing material of the tower.

LOSS OF PLATINUM, AND THE USE OF  
GOLD-LINED VESSELS

Platinum is seriously attacked by concentrated sulphuric acid, especially when traces of nitrous acid are present. This disability has been investigated by Davis,<sup>1</sup> Conroy,<sup>2</sup> Heraeus,<sup>3</sup> and others, various figures being recorded as representing the loss per ton of concentrated acid produced. According to the purity of the acid, the loss by corrosion may be taken to be from 0.2 to 5 g., if

<sup>1</sup> *J. Chem. Soc. Ind.*, 1894, 210.

<sup>2</sup> *Ibid.*, 1903, 405.

<sup>3</sup> *Ibid.*, 1891, 460.

## 56 SULPHURIC ACID CONCENTRATION

93 per cent acid is made, and up to 10 g. when 98 per cent.  $\text{H}_2\text{SO}_4$  is produced.

Heraeus found that alloys of platinum and iridium withstand the action of hot sulphuric acid much better than pure platinum, and that gold is even less attacked. The following figures (as stated by Heraeus) refer to sheets of metal which were allowed to remain forty days in a concentrator producing 98 per cent.  $\text{H}_2\text{SO}_4$  :—

Per cent. Platinum.	Per cent. Iridium.	Per cent. Gold.	Relative corrosion effect.
99.99	0.01	—	100
99.50	0.50	—	90
95.00	5.00	—	73
90.00	10.00	—	58
—	—	100	13

Homogeneously gold-lined vessels were introduced by Heraeus as a result of these investigations. Sheets of the double metal are prepared by heating a bar of platinum to white heat, pouring over this the required amount of molten gold, and subsequently rolling. The relative thicknesses of gold and platinum in the sheets thus prepared vary from 1 :  $1\frac{1}{2}$  to 1 : 8. Vessels built from these double sheets were installed in many German and American works.

Heraeus stills are not suitable for the concentration of anything but pure acid, as the formation of crusts quickly damages the gold lining.



## POSITION TO-DAY

Singularly few platinum stills are worked to-day, and it may be assumed that the use of this metal for acid concentration is now practically obsolete. Johnson, Mathey & Co., Ltd., of Hatton Garden, London, writing to one of the authors on the 26th of August, 1924, said · “ We have not made any platinum pans for a good many years.”

The commercial development of Vitreosil and the silicon irons synchronised with an abnormal advance in the price of platinum, and undoubtedly · hastened the supersession of this one-time popular method of acid concentration

## CHAPTER VI

### CASCADE CONCENTRATORS

THE most popular concentrator of the heated vessel type is that known as the "cascade" system, where either Vitreosil or silicon-iron parts are employed. Vessels of various shapes have been used. Those with which the heavy chemical industry is most familiar are basins of various sizes, some of which are provided with Field tubes (Mackenzie), beakers (Webb), trays, and pans, etc.

Porcelain dishes with glass heads were suggested by Hughes, as also by W. and H. Adams. These suggestions were embodied in U S patents.

Lead pans are only serviceable for the concentration of chamber acid to 80 per cent. strength, and their application is circumscribed. The use of glass retorts for O V. concentration has languished, and now only a few small works perpetuate the system; platinum stills have fallen into desuetude.

There is, however, plenty of activity in cascade plants .

#### EARLY PORCELAIN BASIN CONCENTRATOR

This system apparently owes its origin to Négrier, of Perigueux, who was responsible for B P.'s Nos. 4171 and 14022, of 1890, which cover a plant for concentrating chamber acid to 167° Tw. in basins of Limoges porcelain. These basins were about 12 ins. to 14 ins. diameter, having a depth of from 5½ ins. to 8 ins. They were seated in cast-iron plates, and in many works were protected against

direct heat by a layer of asbestos and a semi-circular perforated cast-iron dish. Interposing the perforated dish or asbestos and the porcelain basin was a layer of siliceous sand. The fire flue was constituted of Volvic slabs, or acid- and heat-resisting tiles placed together in such a way as to reduce the joint to a minimum. The acid to be concentrated flowed from basin to basin in cascade fashion.

Sorel, in his interesting book on "La Grande Industrie Chimique," affords the following additional particulars concerning this installation:—

"On a modifié ce type de fours en supprimant le chauffage par foyer unique, et y substituant le chauffage par trois foyers, alimentés d'heure en heure par une quantité connue et pesée de combustible; dans ces conditions la dépense de capsules et la perte consécutive d'acide sont fortement diminuées

"L'appareil Négrier paraît très apte à concentrer les acides troubles provenant de la tour de Glover; il semble qu'il s'applique particulièrement à la concentration des acides ayant servi à nitrer les composés organiques; l'auteur a constaté que de tels acides permettent de recueillir une proportion considérable de nitrobenzine en tête des appareils de condensation des vapeurs."

#### BEAKER TYPE OF CONCENTRATOR

More than twenty-six years ago, one of the authors was associated with the erection of the

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beaker type of concentrator, based on the Webb's system. Indeed, Webb (and subsequently Levinstein) was responsible for the introduction of glass beakers. Webb's original patent (B.P. 2343, of 1891) had reference to the use of glass beakers supported on slabs arranged in a stepped manner in a heating chamber. These vessels were enclosed towards the top in iron plates or slabs. A loose tapering glass tube was placed in each vessel at an angle of inclination reaching from the spout of one vessel to the foot of the succeeding one. The vessels were approximately 11 ins. diameter by 21 ins high, with overflow lips giving communication to the aforementioned tapered glass tubes, the purpose of which was to bring the strong acid from the vessel above to the bottom of the succeeding one. In this way, concentration was sensibly aided by preventing stratification

With glass beakers the breakages were heavy, and the loss of acid serious. To overcome these defects, porcelain vessels were later introduced.

A typical Webb's concentration plant is shown in Fig. 10. This plant comprises two rows of fourteen porcelain vessels, heated by two fires, the products of combustion from which first pass into combustion chambers on each side of the heating flues, and finally emerge into a space around the vessels. The waste heat is conducted under a lead pan, and then passes to a drop flue leading to the chimney.

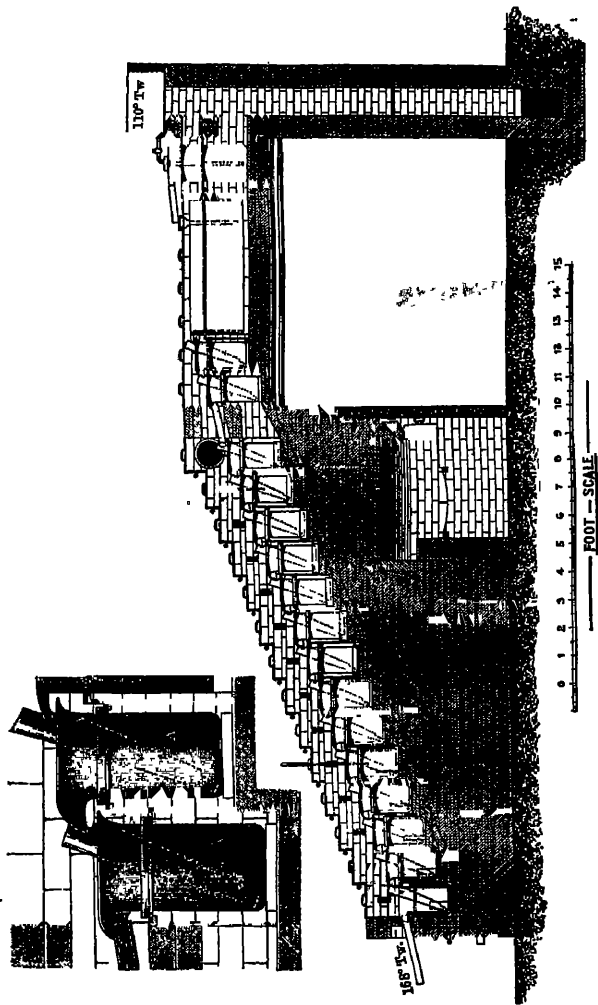


FIG. 10.—WEBB'S CONCENTRATION PLANT.

The Webb's plant with which one of the authors was connected was singularly unsuccessful at the outset, as, indeed, were many other such plants erected in various parts of the country about the same time.

No adequate provision for dealing with the vapours was arranged, the breakages of the beakers were heavy, the fuel consumption was high, and the emission of dense white fumes from the chimney was a source of nuisance to the immediate neighbourhood.

The attempts to rectify the defects were tardy. Much correspondence passed, but few effective steps were taken to place the plant in working order and capable of fulfilling the guarantees originally given. From these early experiences of acid-rectifying plants erected by patentees, two indelible impressions were formed. One was the rule-of-thumb methods of some of the so-called chemical engineers of those times, and the other was the endeavour made to vindicate the efficiency of what was obviously an imperfect and well-nigh unworkable plant.

The vocabulary of one of the authors was singularly enriched as a result of litigation instituted by a company other than the one with which he was connected, consequent on the defective working of a Webb's acid concentration plant. One was familiarised with garnishee orders, interlocutory judgments, and other such technicalities well known to the legal luminaries.

However, space will not allow of a detailed narration of these early reminiscences. Suffice it to say that the failure of the Webb's concentration plant was fairly general. The broad upshot of the litigation was that firms who had installed the Webb's system secured no monetary recompense, and they had to put their respective installations in working order themselves.

#### MODIFICATIONS TO THE ORIGINAL WEBB'S CONCENTRATOR

At the works with which one of the authors was connected, the modifications made to render the plant workable were these :—

(1) Larger preheating lead pans were erected.

(2) (a) A modified type of condenser of larger capacity for the condensation of the acid fumes arising during the concentration was provided; (b) three outlets from each of the stepped beds were taken into a common pipe, which was water-cooled, and which led, in turn, to the condenser.

(3) A more efficient acid cooler was provided.

With the foregoing modifications, it was possible to produce C.O V of 94–95 per cent. strength without occasioning nuisance in the neighbourhood, and without undue loss of acid from breakages, but the yield scarcely ever exceeded 28 carboys—2·2 tons of C.O V.—per day, whereas

the installation was originally intended to produce 5 tons of C.O.V. per day.

#### OPERATION OF THE PLANT

Prior to starting the plant, it was necessary to fill the two sets of 16 porcelain beakers with B.O.V. About a ton of acid was required for this purpose. A slow fire was started, until the temperature of the acid reached  $180^{\circ}\text{C}$ ., in the last beaker. Four to six hours were occupied, according to the condition of the plant, in attaining this temperature. The fires were then judiciously forced, and the feed of acid started.

The control of the plant from this point depended on the temperature of the acid in the final beaker, which was  $295\text{--}300^{\circ}\text{C}$ ., on the strength of the concentrated acid emerging from the plant, which was  $166\text{--}168^{\circ}\text{Tw.}$ , and on the strength and temperature of the acid in the lead pans. It was also important to note, two or three times per shift, the yield and specific gravity of the weak acid collected at the condenser. The charging of the fires was done regularly, and efforts were made to avoid the introduction of an undue volume of cold air.

The Webb's concentration plant, modified in the way outlined, continued to work for several years, and was not replaced until 1909, when the merits of Vitreosil were fast gaining currency.



## VITREOSIL BASIN CASCADE CONCENTRATOR

It was early in 1909 that the company with which one of the authors was associated received from the late Dr. Bottomley, of the Thermal Syndicate, Ltd., a letter in the following terms:—

“The Benker-Hartmann basin type of cascade concentrator has proved most efficient for the manufacture of water-white acid. Silica basins, which were ~~put~~ <sup>were</sup> on the market nearly three years ago, have improved the yield and working costs of the plant to a marked extent, owing to the absence of fire-brick slabs underneath the basins. With porcelain basins a 3-in. slab was usual, but with silica basins it is now necessary to seat the basins in an asbestos ring, which are inset in a fireclay slab.

“We enclose some figures of a plant using our basins, which has been recently erected. The price of the silica parts for a set similar to this is as follows:—

	£	s	d.
40 basins @ 18s. 9d. each . . .	37	10	0
3 cooler units @ £3 each . . .	9	0	0
2 “D” pipes @ 11s each . . .	1	2	0
	£47	12	0

“The cost of the plant and erection will, of course, depend on the acid concentrated. If Glover acid is used, no preheating pans will be

required, so that the cost of firebricks, slabs, furnace, and erecting should not be more than £100. The total cost would be between £150 and £200.

"With three preheating pans the cost would be increased by about £50. We have lately prepared drawings of a plant similar to the basin one ~~in~~ design, but adapted for concentrating smaller quantities of acid.

"We enclose a sketch of the proposed arrangement, showing four units only. The cost of silica parts only for a 15-unit plant of this type would be £40,

in which the re that boiling over is impossible and the acid is absolutely clean.

"The yield of acid would be proportionate to the yield of a basin plant; that is to say, 15 units would give about fifteen-twentieths of a 40-basin plant."

The use of open slabs, with provision for asbestos rings on which the silica basins rested, to which the late Dr. Bottomley made allusion in the letter in question, marks a distinct advance on anything hitherto achieved. This progressive step was due to the remarkable properties of Vitreosil, to which full reference has been made in Chapter II.

## VITREOSIL BASINS AND SEATING TILES

Fig. 11 illustrates the silica basins, trays, and pipes as made by the Thermal Syndicate, Ltd.

In Fig. 12, details are afforded of Davison's

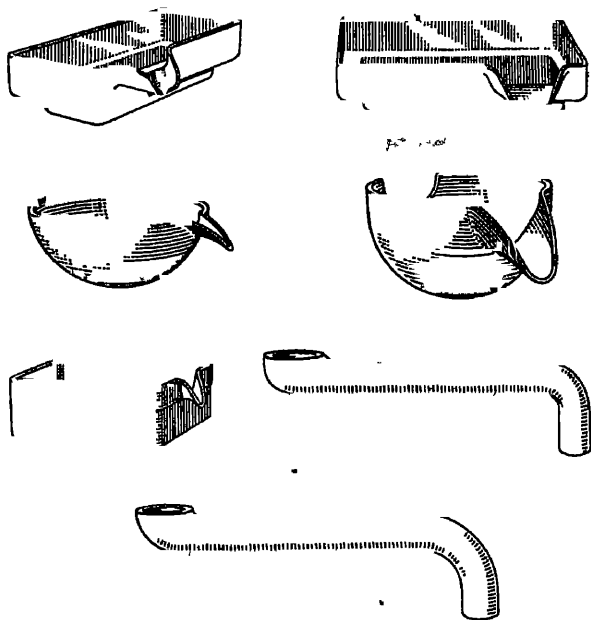


FIG. 11.—VITREOSIL BASINS, TRAYS, AND PIPES.

basin and tray-seating tiles, which are now almost exclusively used in the erection of cascade concentration plants.

In forming a complete cascade flue, three types of seating tiles are used. Immediately above the

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furnace, tiles with solid bottoms are employed, usually three or four in each row. These are followed by three perforated seating tiles, and then subsequently by the open type, which affords a comparatively large surface for direct action of the heat of the products of combustion on the

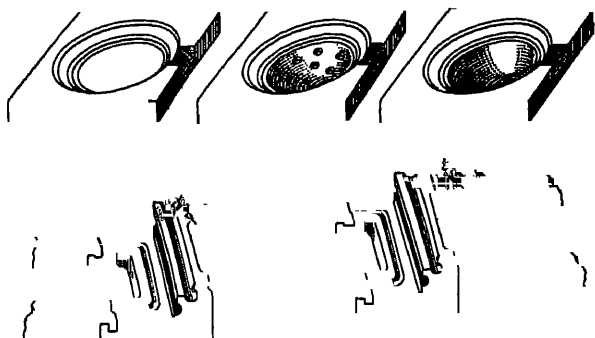
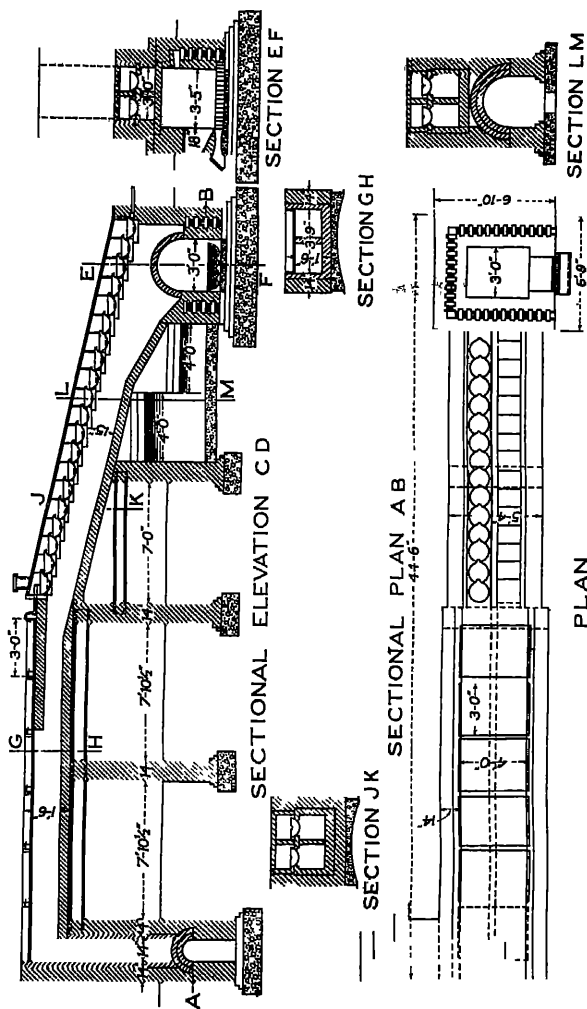


FIG. 12.—OBSIDIANITE BASIN, AND TRAY-SEATING TILES.

### ORIGINAL TYPE OF VITREOSIL CASCADE CONCENTRATION PLANT

Fig. 13 affords details of the original type of Vitreosil cascade concentration plant, erected by one of the authors, following the receipt of the late Dr. Bottomley's letter, mention of which has already been made.

The plant in question comprised two rows of twenty basins each, and six lead preheating pans. An innovation was adopted in the form of a small



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forced-draught furnace for the combustion of breeze, which was demonstrated by practical working to be very satisfactory, as it possessed a resiliency not common to most open-type furnaces hitherto used in connection with cascade plants.

The cost of the plant, which was connected to an existing condenser (used previously in conjunction with the Webb's plant), was as follows —

	£	s.	d.
7000 common red bricks and 200 common red side arch bricks	16	0	0
Rolled steel joists	4	0	0
Bracing members, tie rods, and damper plates	10	0	0
Special seating tiles, 20 A type, @ 8s. each	8	0	0
" " " 40 B " @ 1s. 6d. each	3	0	0
" " " " @ 4s. 6d. each	4	1	0
Two @ £3 each	6	0	0
40 Vitreosil basins, @ 18s. 9d each	37	10	0
6 Vitreosil D pipes, @ 11s. each	3	6	0
Labour involved in the erection of the plant	35	0	0
Forced-draught furnace and equipment	10	10	0
Lead pans and cast-iron plates	42	10	0
Firebrick squares and side arch bricks	21	7	6
Concrete and excavation	12	5	0
Drain-pipes, asbestos insets, water- and steam-pipes	20	0	0
<b>Total</b>	<b>£233</b>	<b>9</b>	<b>6</b>

It should be remarked that the flue to the chimney already existed, and that very little expense was incurred in connecting to the existing lead trunk which afforded access to the condenser.

In any case, it will be conceded that the cascade plant in question was a comparatively cheap one, when contrasted with concentration units of the Webb's type.

The plant produced 3.9 tons of C.O.V. per day from chamber acid of 106° Tw., and the yield of weak acid from the condenser, taken over a prolonged period, averaged 192 c.c. per minute. The specific gravity of the weak acid was 1.24. By calculation, the following figures are arrived at:—

Weight of relative qualities of acid.			Specific gravities of acid	Percentage of $H_2SO_4$ .	Tons of mono- hydrated sulphuric acid.	Relative percent- ages.
T.	c.	q. lb.	° Tw.			
	6	2 20	48	32	0.168	4.33
3	18	0 0	168	95.0	3.705	95.66
						100.0 (say)

The consumption of breeze, having a calorific value of 9500 B.Th U.'s per lb., was 8 cwt. per ton of C.O.V. produced. It was found necessary to clinker the forced draught furnace twice each twenty-four hours

#### LATER IMPROVEMENTS

As a result of the continued operation of the foregoing plant, several improvements were introduced. The following detail the more important:—

(1) The use of lead covers for the cascade in lieu of acid- and heat-resisting tiles hitherto employed.

These covers were made of 12 lb. chemical sheet lead, and were suitably strapped to a light

pitch-pine framework. Provision was made immediately above each basin for a dipping hole, so that, in the event of broken basins being suspected, a means of locating them was readily available.

It was the absence of means for detecting tilted, fractured, or broken basins, and the inconvenience in the handling of the acid-resisting cover tiles which was responsible for the adoption of the lead covers, which possessed the merit of lightness and durability.

(2) A water-jacketed lead box was used for cooling the acid vapours issuing from the cascade.

Experiments revealed that except the temperature of the gases was reduced at once, destruction of the lead trunk pipes leading to the condenser was very rapid.

A water-cooled box made of 18 lb. chemical sheet lead, 3 ft 6 ins. long by 2 ft. 6 ins. wide by 2 ft. 6 ins. deep, was placed on four Obsidianite splits inside a lead-lined box. The acid vapours were introduced to the box by two 6-in. diameter special connections, each comprising two pipes, one a spigot and socket straight pipe, and the other a spigot and socket quarter bend, both made of silicon iron. Collars with suitable packing were used, so as to secure tight joints at the water jacket and the fume box.



The cooling box was supported on horizontal steel channels carried on vertical channels, which served to brace the plant. A 9-in. diameter lead pipe of 16 lb. lead served to convey the acid vapours to the condenser. A lead pipe of  $\frac{1}{2}$  in. diameter, suitably sealed, led the weak condensed vapour to the condenser. The specific gravity of this acid was invariably  $8^{\circ}$  Tw. A continuous feed of water was maintained on the box, and the reduction of temperature was such that destruction of the lead trunk pipes was obviated.

(3) It was soon found that the Vitreosil pot type cooler surrounded by water in an outer lead vessel was unsatisfactory for cooling the resultant C.O.V., and it was necessary to provide a modified arrangement of cooler for each bed, details of the design of which are indicated in Fig. 14.

(4) Another defect which revealed itself at an early period was that additional protection was necessary for the first and second lead preheating pans. Originally, only one course of firebricks was placed on the top of the cast-iron plates.

In diverting the flow of the products of combustion from an inclined to a horizontal plane, a pronounced impingement takes place on the first and second lead pans, and it is essential that these should have a protection of

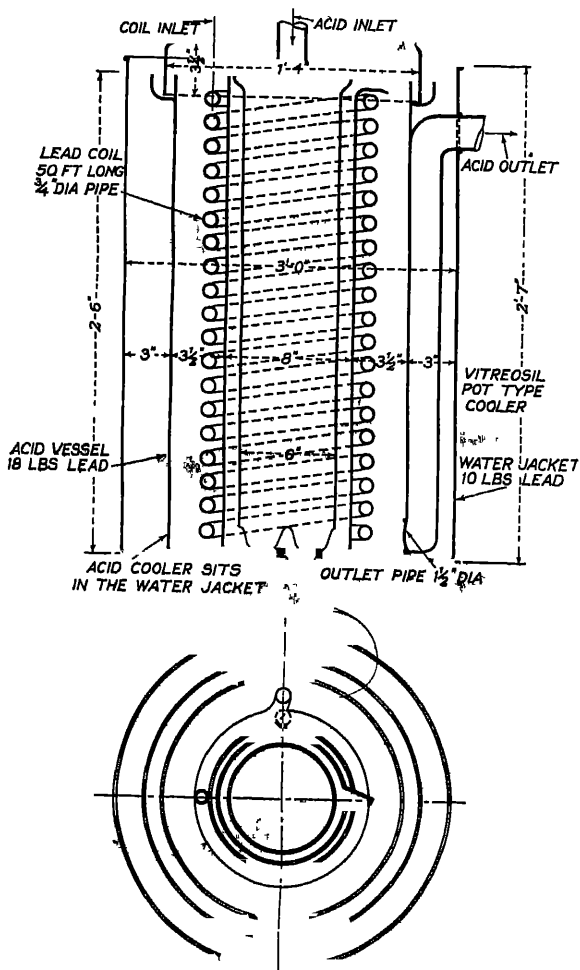


FIG. 14.—AOLD COOLER.

at least 6 ins. of firebrick, if leakages are to be avoided.

A cascade plant arranged on the lines of the original installation under consideration, embodying the modifications just enumerated, will prove an efficient and foolproof one, given careful control.

### DEVELOPMENTS

A later development was the introduction of Vitreosil trays in lieu of lead pans. One such plant, comprising fifty basins and thirty trays, practically the first of its kind, was erected by one of the authors and his colleague at that time (J. F. Carmichael, B.Sc., F.I.C.), at Glasgow, early in 1912. This plant constituted an advance on previous installations erected.

About this period a controversy arose on the subject of the intrinsic merit of silica trays for acid concentration as compared with lead pans.

In this connection it is important to note that everything depends on the condition and tightness of the asbestos rings on which the trays are seated. If the rings have become friable, or have "wasted," it will be found that cold air is introduced, and cools a relatively large surface area of the tray.

Given tight joints at all times, silica trays may prove more efficient than lead pans.

A trial was made at a works in Glasgow, where two cascade plants were operating under identical

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conditions, side by side. One plant comprised lead preheating pans having an area of 64 sq. ft.; the other plant consisted of silica tray preheaters having an area of 60 sq. ft. The respective plants produced 3.5 tons and 3.4 tons of 168° Tw. acid per day. It was found impossible to increase the productivity of the unit having lead pan preheaters without injury to them.

Although the result of the trial in question indicated that a greater quantity of water was evaporated per square foot of silica tray surface than per square foot of lead pan surface, the improvement was not appreciable.

Other workers have affirmed that the most efficient and economical method of concentrating chamber or dearsenicated sulphuric acid to 140° Tw was in open lead pans, working on the continuous-flow system.

No doubt justification exists for the latter dictum. But the authors have had experience of several concentration plants where it was revealed that lead pans constituted a limiting factor to the quantity of acid to be concentrated. In other words, it was possible to force judiciously a concentrator having silica tray preheaters because it possessed a certain elasticity as regards productive capacity, but with lead preheating pans there is a well-defined limit to the capacity. If this limit is exceeded, damage to the lead-work is caused.

Another factor of importance in this connection needs to be considered. Vitreosil trays are more than three and a half times as expensive as lead pans. The latter have a distinct salvage value after use, whereas broken silica ware has little, if indeed any, salvage value at all. The question of capital expenditure, as also the value which can be realised for the plant after its effective life has ceased, are obviously considerations of importance.

### MODERN PLANT

Modern Vitreosil cascade concentrators are provided with beaker preheaters. These have been adopted on account of the greater heating surface and smaller cooling area. Clearly, more intimate contact with the products of combustion is secured than is possible with the shallow trays.

Fig. 15 furnishes all the essential details of the modern concentrator in question.

It is usual to erect this plant in 5 and 10 ton units, the first consisting of 30 beakers and 50 12-in basins, the second comprising 60 beakers and 100 basins.

The Vitreosil vessels are placed on specially designed acid- and heat-proof seatings, recessed to receive asbestos cord rings, which serve to afford a tight joint between the products of combustion and fume flues.

Reference to Fig. 15 will show that an ordinary

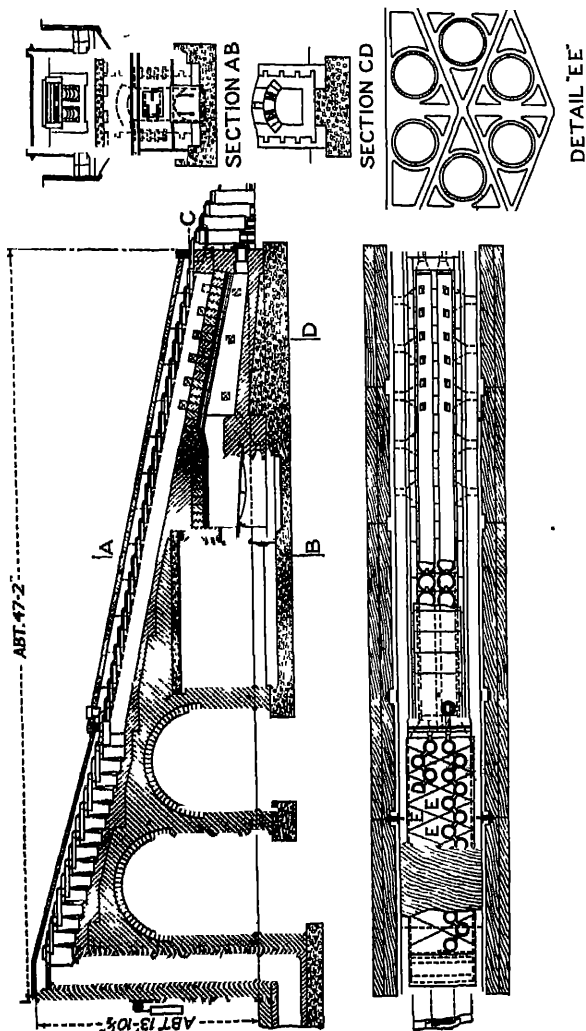


FIG. 15.—MODERN SULPHURIC ACID CASCADE CONCENTRATION PLANT.

open firebar furnace is fitted under a pigeon-holed arch, from which the flue runs the whole length of the plant, finally leading to the chimney. This arrangement is designed to ensure isolation of the products of combustion throughout the concentration, in order that the condensation loss will be low, and the finished acid will be of water-white quality.

Low-grade fuel, or slack, is generally used. The fuel consumption is 15 to 20 per cent. of the weight of the final acid produced.

Plants comprising 30 beakers and 50 basins have an output of 5 tons of 168° Tw. acid per twenty-four hours, commencing with a cold feed of 106–110° Tw. chamber acid.

The 10-ton units are merely two 5-ton sets assembled with a 9-in. dividing wall. They are fired separately.

#### COMPARATIVE WORKING RESULTS ON TRAY AND BEAKER PLANTS

Reference has already been made to the advantage which the beakers possessed over the trays. This advantage is emphasised by the following results :—

*Plant A.* Five-ton plant, having 50 S.I basins and 30 right- and left-hand trays, using chamber acid

*Plant B.* Ten-ton plant, having 100 S.I basins and 60 beakers, using chamber acid, as above.

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Plant A.		Plant B.	
Inlet of trays :	70° F. 106° Tw. 20° C. 50° Bé.	Inlet of beakers.	90-100° F. 106° Tw. 33-37° C. 50° Bé.
Outlet of trays :	235° C. 110° Tw. 112° C. 51·2° Bé.	Outlet of beakers :	342° F. 130° Tw. 172° C. 56·9° Bé.
Outlet of basins :	168° Tw. (at 60° F.) 85·9° Bé. (at 15° C.)	Outlet of basins :	168° Tw (at 60° F.) 85·9° Bé. (at 15° C.)
O.V. made per 24 hrs.	4 tons.	O.V. made per 24 hrs.	10 tons.
Fuel used per ton O.V.	4½ cwt.	Fuel used per ton O.V.	4 cwt.

It will be observed that there is an increase of temperature ranging from 33-37° C. to 170° C., and as 15 beakers are involved, the increase of temperature per beaker is 9° C.

It is advisable to enclose beakers Nos. 11 to 15, as rapid ebullition takes place, with the evolution of appreciable quantities of acid vapour. The necessity for the latter course will, no doubt, be appreciated when the following observation is recalled. Wherever an attempt is made to pass products of combustion from an inclined to what is virtually a horizontally stepped travel, it will be found that a sensible impingement takes place on the first few elements. This phenomenon has been observed by the authors repeatedly.

### OBSERVATIONS ON THE OPERATION AND CONTROL OF THE MODERN CASCADE CONCENTRATOR

Assuming that the brickwork of the plant has been dried, and that the basins have been filled with the strongest acid available, a small fire should be started, and the temperature of the acid in the basins gradually increased. It is judicious to use at least two recording thermographs of the Cambridge and Paul type, one of



which is placed in one of the basins immediately over the furnace, and the other in one of the beakers immediately adjacent to the basins.

Obviously, at the outset of the operation of the plant, acid below  $168^{\circ}$  Tw. will be produced, and provision should be made for blowing such acid to a suitable storage receptacle.

Acid below 80 per cent. strength can be mixed with the acid above that strength, and in most cases disposed of as B.O.V., to be charged on the basis of the actual content of  $\text{H}_2\text{SO}_4$ .

Five to six hours will be required in which to raise the acid to  $168^{\circ}$  Tw., assuming the plant is being restarted. Where a plant is being operated for the first time, it is unwise to force the plant unduly. From thirty-six to forty-eight hours is a reasonable time in which to attain the required final strength of acid.

It pays handsomely to use a good quality of fuel. Graded coke can be used with advantage. A small quantity of steam should be applied continuously to the firebars of the open hearth type of furnace, in order to prevent the formation of clinker. In this way cleaning can be effected rapidly, and this is a vital factor if breakages are to be avoided and maximum production is to be secured.

It is not generally realised that the labour involved in the operation of cascade concentrators is a serious item, but, broadly speaking, an increased

capacity per concentrator per unit of time does not correspond to a proportionate increase in wear.

Thus an improvement of output is of significance, both from the points of view of labour, and repairs and maintenance.

As the concentration of chamber acid to C.O V. is essentially an evaporation operation, during which water vapour is removed along with dissociation products of the acid to be concentrated, it is clearly desirable to remove the water as rapidly as possible. In this connection, the importance of the maintenance of a reasonable draught on the fume flue is obvious. This is the more significant when regard is had to the character of the joint used for obviating inter-communication between the two flues—the products of combustion flue and the fume flue.

There are, undoubtedly, times when the asbestos insets become worn, and incapable of preventing the passage of the contents from one flue to the other.

As the products of combustion flue invariably has the same source of draught as the vapour flue, and as the former has an uninterrupted passage, whereas the acid vapours have to overcome the resistance of the coke packing of the condenser, it is certain that acid vapours will pass into the products of combustion flue should a joint become unsound. This is the explanation of the "white

chimney," which is well known to those who operate cascade plants.

"White chimneys" can be avoided in two ways. Firstly, there should be a periodic inspection of the asbestos insets, and those which show signs of wasting should be renewed. Secondly, it is vitally important that the fume or vapour flue should be operated under slightly greater suction than obtains in the products of combustion flue. Where the source of draught is from the same chimney, manifestly to create a greater suction in the fume flue involves one of two things. Either a steam jet should be used in the condenser outlet, or a Kestner regulus metal fan should be employed at the outlet of the condenser. The authors prefer the latter.

By adopting this measure, not only is loss of acid avoided, and the possibility of a "white chimney" reduced to a minimum, but the capacity of the concentration plant will be sensibly increased, because a positive step has been taken to remove the water vapour, without which maximum concentration is impossible.

It is true that by the use of coal a long flame is secured, and more even distribution of heat throughout the cascade flue is attained. This will not be denied, but with graded coke there is no possibility of soot forming a protective layer on the basins, and moreover, if a closed type of furnace is used and gaseous firing is resorted to, it will be possible to secure ignition of the producer

gas at any point desired. Thus uniform heat distribution can be achieved.

The use of outside producer-gas plants is a method which might with advantage be popularised. Equally, oil firing is worthy of consideration, especially if a suitable cheap grade of oil can be procured.

The basins should be inspected from time to time for the deposition of basic ferric sulphate, as it is known that these accumulations occur, especially where Glover tower acid or dust-containing acid is employed. The presence of basic ferric sulphate in beakers containing acid undergoing concentration causes bumps, and is a prolific cause of fractured elements

#### “IRONAC” CASCADE CONCENTRATION PLANT— HAUGHTON-TUNGAY PATENT

In Fig. 16, the general features of an “Ironac” plant are shown, constructed in series, having a production capacity of 5, 10, or 20 tons of C.O.V. per twenty-four hours, according to the size of the plant employed.

All the parts in contact with the acid are made of “Ironac” acid-resisting iron. The preheating of the weak acid, which is cold when it is fed into the plant at a density of (say) 108–110° Tw., is dealt with in a series of rectangular trays, with outlet lips arranged alternately right and left hand, in such a way that the acid has a long traverse

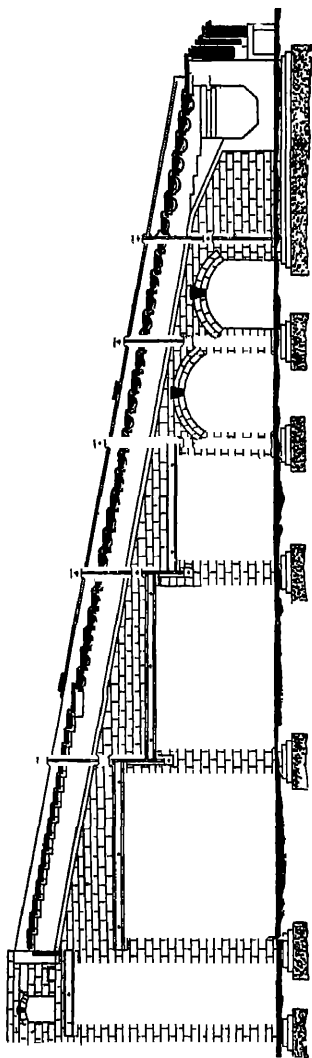


FIG. 16.—HAUGHTON'S "IRONAC" CASCADE CONCENTRATION PLANT INCORPORATING THE  
HAUGHTON-T'UNGAY PATENTS.

over the flue gases, until it is introduced by means of a delivery pipe into the cascade basins for further concentration.

The preheating trays are arranged uncovered, and are always open to inspection. Objectionable fumes are not evolved on this section of the plant.

The concentration proper takes place in the cascade basins. All these are of the standard "Benker" size, but a modification in the design has been introduced. The basins have corrugated upper edges to allow of a free expansion and contraction while under heat, and prevent any overflow or leakage by reason of the frothing of the acid during concentration. The cascade basins are covered, and provision is made for the removal of the acid vapours, through a series of fume pipes to condensers or scrubbers.

The concentrated acid of 168° Tw. is discharged through beaker pipes into a system of pot coolers, or coils around which cooling water is suitably circulated.

These pot coolers are efficient, as "Ironac" has a higher heat conductivity than pottery or other Ceramic material.

The preheating trays have side outlets, and are arranged alternately, as has been indicated already. The Haughton-Tungay "Ironac" basin is fitted with a projecting curtain, the function of which is to prevent any possibility of short-circuiting, by

causing the strong acid to be sent to the lower part of the basin before being discharged.

In this way, all the acid is brought into contact with the heating medium, and can only pass the succeeding basins after maximum concentration has been secured.

Fig. 17 represents the latest design of "Ironac" plant, adapted for the concentration of waste acids from nitration plants in connection with explosives, gun cotton, T.N.T., aniline, and other such processes. This plant embodies several improvements.

At the outset the waste acid must be denitrated. This is a separate operation, involving the use of steam or superheated gases, which are brought into contact with the waste acid on a counter-current principle in denitration towers.

The denitrated acid is fed to the top of the cascade for primary treatment in the preheating trays, and then subsequently to the basins, which are enclosed, as it is at this section of the plant that slight dissociation of the acid is likely to occur. Provision is made for conveying the acid vapours *via* suitable fume pipes to the condenser.

As soon as the acid is concentrated sufficiently to obviate corrosion of cast iron, *i.e.*, to a strength of about 92 per cent.  $\text{H}_2\text{SO}_4$ , it is conducted *via* a beaker pipe to a large shallow rectangular cast-iron pan, fitted with a removable cover. In this

causing the strong acid to be sent to the lower part of the basin before being discharged.

In this way, all the acid is brought into contact with the heating medium, and can only pass the succeeding basins after maximum concentration has been secured.

Fig. 17 represents the latest design of "Ironac" plant, adapted for the concentration of waste acids from nitration plants in connection with explosives, gun cotton, T.N.T., aniline, and other such processes. This plant embodies several improvements.

At the outset the waste acid must be denitrated. This is a separate operation, involving the use of steam or superheated gases, which are brought into contact with the waste acid on a counter-current principle in denitration towers.

The denitrated acid is fed to the top of the cascade for primary treatment in the preheating trays, and then subsequently to the basins, which are enclosed, as it is at this section of the plant that slight dissociation of the acid is likely to occur. Provision is made for conveying the acid vapours *via* suitable fume pipes to the condenser.

As soon as the acid is concentrated sufficiently to obviate corrosion of cast iron, *i.e.*, to a strength of about 92 per cent.  $H_2SO_4$ , it is conducted *via* a beaker pipe to a large shallow rectangular cast-iron pan, fitted with a removable cover. In this



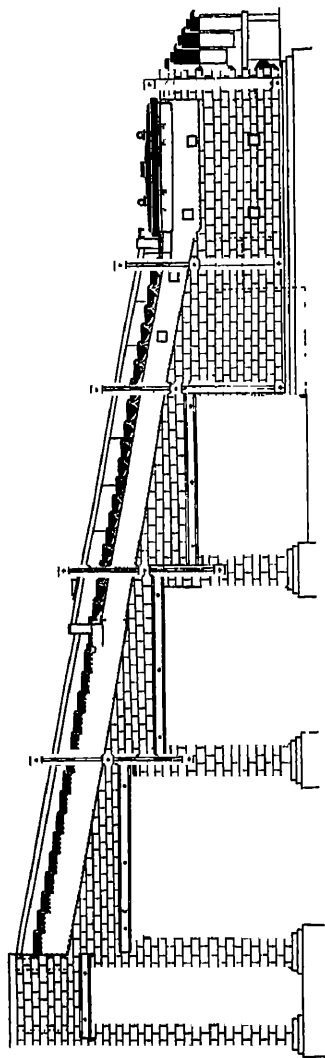


FIG. 17.—HAUGHTON'S "IRONAO" CASCADE CONCENTRATION PLANT FOR RECONCENTRATING WASTE ACIDS.  
10-TON PLANT. INCORPORATING THE HAUGHTON-TUNGAY PATENTS.

pan the final concentration to 96–97 per cent.  $\text{H}_2\text{SO}_4$  is effected.

The cover of the cast-iron pan is provided with a separate outlet for the acid vapours. In concentrating to the high strengths named, distillation, as distinct from concentration, occurs to some extent, and it is advisable to have a separate lead to the condenser. In point of fact, a separate condenser has been found desirable in some cases.

After emerging from the cast-iron still, the rectified acid is discharged by a beaker pipe into a series of coolers, which are water-cooled.

From time to time it is necessary to remove the cover of the pan, so that any accumulated solid matter deposited from the waste acid can be removed.

The installation in question has a capacity of approximately 10 tons of concentrated sulphuric acid per twenty-four hours, when basing on a finished acid of 97 per cent.  $\text{H}_2\text{SO}_4$ .

A plant which combines the merits of high yield and compactness is shown in Fig. 18. At some chemical works ground space is limited, and plants of the type in question are appreciated. They are adapted for the concentration of chamber acid or waste acids

Visibility is always a merit of any type of chemical plant, and particularly is this the case with an acid concentration plant. Fig. 19 illus-

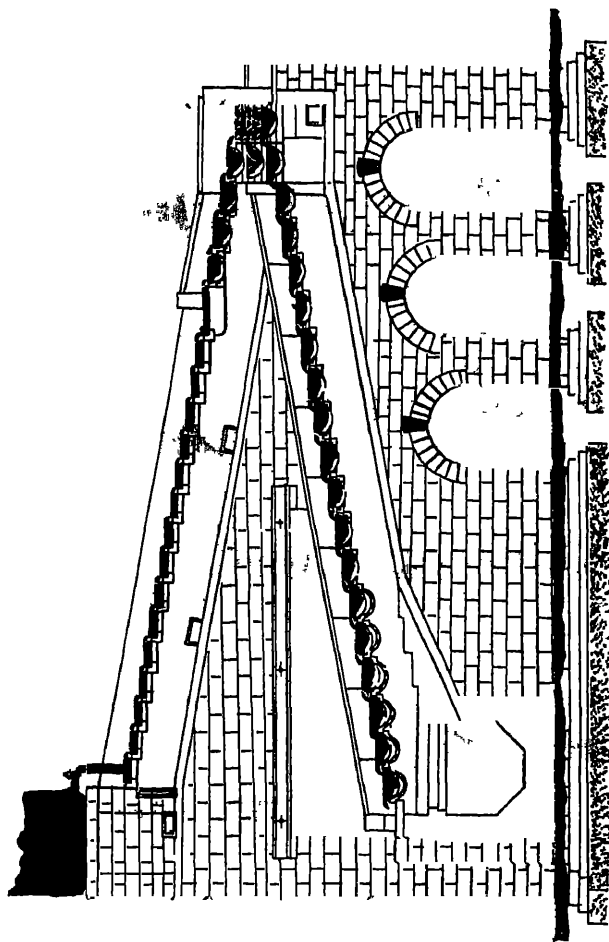


FIG. 18.—HAUGHTON'S "IRONAC" CASCADE CONCENTRATION PLANT, COMPACT TYPE.

trates a series of 36-in. diameter shallow pans, made of "Ironac," seated in a cascade manner, so as to constitute an acid concentration unit.

Each pan has a socketed inlet and an overflow lip, or outlet, arranged at a suitable level for discharging the acid in the course of concentration. Each pan is also provided with a separate removable cover, to which is attached a fume pipe for withdrawing the acid vapours.

The fume pipes leading from each of the covers are connected to a main water-jacketed pipe for the removal of the acid vapours to the condenser.

It is understood that the working of this type of plant has been very satisfactory.

Fig. 19 shows a unit which has proved to be capable of an output of 10 tons of C.O.V. of 168° Tw. per twenty-four hours, with a feed of chamber acid of 110° Tw.

It will be realised that one of the features of the pans illustrated is the large heating surface in constant contact with the products of combustion, and with an effective conducting material, such as "Ironac" and the other silicon irons generally are, very effective concentration is possible

The plant under review possesses additional features in that it entails a minimum of brickwork, and occupies considerably less ground space than many other types of cascade plant.

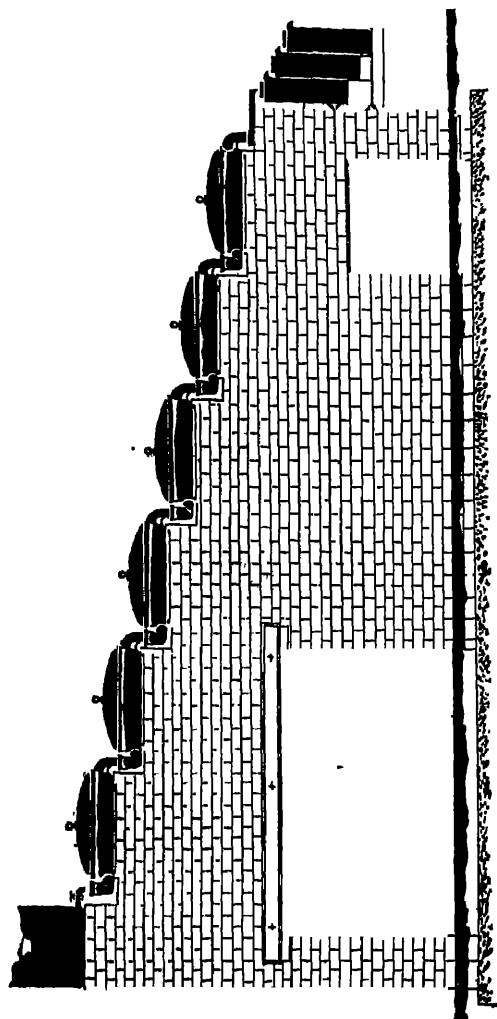


FIG. 19.—VISIBLE TYPE "IRONAC" CASCADE CONCENTRATION PLANT. 10-TON PLANT.

Fig 20 represents a concentration unit patented by Beck and Bithell, of Belfast, a few years ago. A concentrator on this principle was erected at Beck's works at Belfast.

The products of combustion traverse a central flue formed by the column of cascade dishes, or rings. Suitable provision is made in the form of a lead tower to surround the entire nest of circular vessels, with the object of collecting the fumes evolved during concentration. The "Ironac" dishes nest one upon another, and are virtually in the form of rings, with a large annular central space, which forms a central flue, and the dishes, or rings, are stacked one upon another. Each of the separate rings has an overflow notch, as shown, and a collector with a lip is placed at the bottom of the stack.

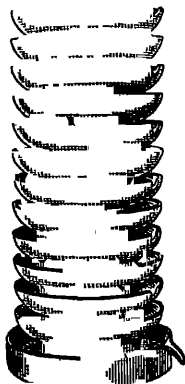


FIG. 20.—IRONAC  
"BECK AND BITH-  
ELL" ARRANGE-  
MENT.

## "TANTIRON" AND "NARKI"

### CONCENTRATORS

Both the Lennox Foundry Co., Ltd., of New Cross, London, S.E.14, and John Varley and Sons, Ltd., of St. Helens, Lancs., supply complete

cascade plants, designed on similar lines to some of those already described.

### CONDENSERS

The size of the condenser for a given weight of finished acid depends on the type of concentrator used—that is, whether of the heated vessel or hot gases type.

In the latter system, the condensers of which are dealt with on pp. 81 and 83 of the first volume, not only has this piece of apparatus to deal with a larger volume of gases, inasmuch as the products of combustion pass along with the acid vapours, but the temperature of the mixed gases is usually higher.

It has been found necessary to provide four to five hundred cubic feet of packing per ton of finished C.O.V. with the hot gas type of concentrator, whereas with the heated vessel type, from 60 to 100 cu. ft. per ton of finished C.O.V. will suffice. The authors recommend the cooling of the acid vapours with water or weak acid, or a combination of the two, prior to the vapours being led to the condenser. In this way, more complete condensation is ensured, and destruction of the lead pipes leading to the condenser is avoided.

Fig. 21 shows a typical condenser, adequate in size for a cascade plant producing 4 tons of C.O.V. per day. It will be seen that this consists of a timber framework, wood-lined, and subsequently lead-lined with 12 lb. lead. Particulars of the various grades of coke are shown, as also is

the method of removing the condensed acid, which is led to one of the weak acid pans or beakers,

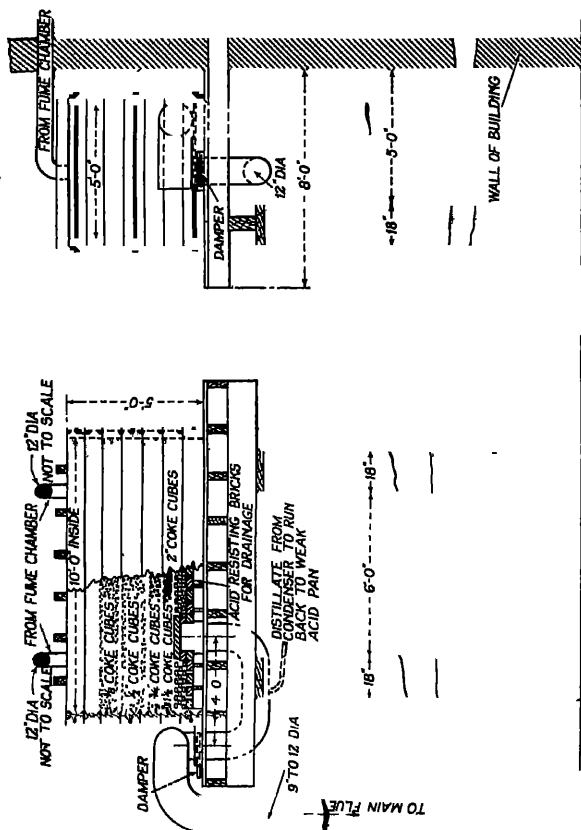


FIG. 21.—CONDENSER FOR CASCADE CONCENTRATING PLANT.

according to the character of the plant used Hard metallurgical coke is preferable as a packing medium.



## CHAPTER VII

### CONCENTRATION IN CAST-IRON POTS

For the concentration of acid of 92-94 per cent. up to 96-98 per cent. cast-iron vessels may be employed. In the case of such concentrations, which necessitate high temperatures, the use of glass is impracticable, and platinum is subject to appreciable wear and tear.

Cast-iron pots were largely used in conjunction with glass or platinum stills, the acid being first brought up to about 93 per cent. in the latter vessels, and finally concentrated to the required strength in some form of cast-iron pot or retort. At the present time, when platinum and glass are rarely employed, the use of pots usually follows cascade concentration, or one of the "direct heat" systems.

Generally speaking, cast-iron concentrators take the form either of deep pots or shallow pans, provided with cast-iron or lead covers, and are used in connection with suitable condensers and scrubbers to deal with the products of dissociation. Such apparatus has been the subject of a number of patents, but many of these have not been practically applied, or only at the place of their origination.

Cast-iron pans have been employed in the Faure-Kessler system, in which the cover is a water-cooled lead bell. In this case the rim of the pan is protected from the action of the weak acid

which condenses in the cover, by the provision of a platinum apron piece. Cast-iron pans with platinum domes have also been used (Ger. P. 61331) in this system.

Another method employs long pans about 10 ft. by 2 ft., with lead covers. These vessels are charged with 96 per cent. acid, which is heated to  $240^{\circ}\text{C}$ . Concentration up to 98 per cent.  $\text{H}_2\text{SO}_4$  is obtained by blowing a stream of hot air over the surface of the acid. The concentrated acid is then allowed to cool, or is discharged through suitable coolers, but sufficient is left in the pan to allow of feeding with 94 per cent. acid without reducing the charge below 96 per cent  $\text{H}_2\text{SO}_4$ .

Herreshoff, H. Nichols, and G. Nichols have patented a process (B P. 1998, 1897) in which the concentration of 86 per cent up to 98 per cent.  $\text{H}_2\text{SO}_4$  is carried out in two stages. The acid is made to take a zigzag course through two special cast-iron pans. In the first of these, concentration up to 96 per cent.  $\text{H}_2\text{SO}_4$  takes place, while the second is heated to such an extent that 50–60 per cent. of the acid is dissociated, the residual acid being 98.5 per cent.  $\text{H}_2\text{SO}_4$ . The vapours from the second vessel condense to produce 93.5 per cent acid.

Several methods have been suggested whereby acid of lower strength than 92 per cent.  $\text{H}_2\text{SO}_4$  may be concentrated in cast-iron apparatus. In

## 98 SULPHURIC ACID CONCENTRATION

such systems, the weak acid is run on to the surface of boiling acid of higher concentration, or is prevented from attacking the pot by the provision of shields of stoneware or high silicon iron. Such a process is that described by the Clayton Aniline Co., Ltd., in B.P. 11544, of 1898.

Cast-iron pots are sometimes used in conjunction with an enclosed cascade made up of shallow dishes. Details of this type of plant may be found in B.P. 127652, 1917 (Morgan), and B.P. 101642, 1916 (Dreyfus).

By the use of recuperator towers in cast-iron pot concentration, advantage is taken of the heat of the vapours arising from the pot to preheat the feed acid. Dreyfus and the Clayton Aniline Co., Ltd., describe the use of a packed tower for this purpose in B.P. 788, 1902

The following details refer to an improved type of Dreyfus cast-iron concentrator which was erected in 1916 at a metropolitan chemical works.

The general arrangement of the plant is indicated in Fig. 22. Four such units were erected, each comprising a Dreyfus cast-iron pot, cooler, and recuperator tower, and having a common fume-collecting box and graded coke scrubber.

Wrought-iron storage boilers were arranged to receive the acid to be concentrated from railway tank wagons, and an overhead lead tank was constructed, so that this acid could be fed to the recuperator by gravitation. Elevation of the acid

was effected by means of compressed air, an iron egg being coupled to the storage boilers for this purpose. Special feed boxes were provided,

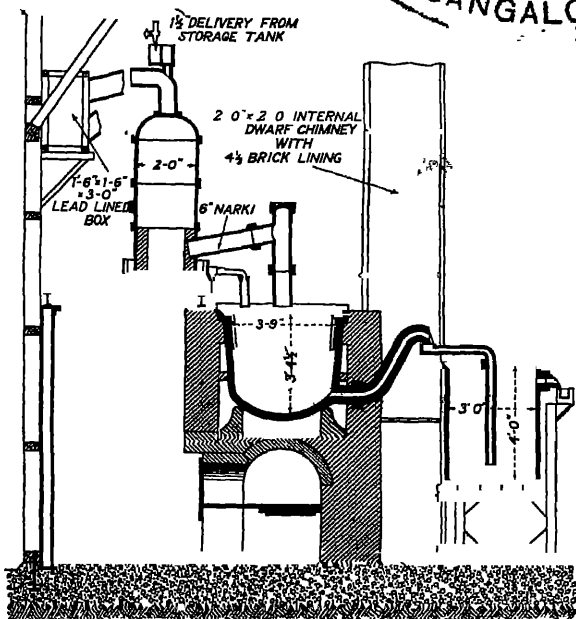


FIG. 22 —GENERAL ARRANGEMENT OF A DREYFUS PLANT.

to allow of delicate adjustment of the flow of acid to the recuperators.

The recuperator towers served a double purpose. They preheated the cold acid prior to its introduction to the pots; and secondly, they partially cooled the products of evaporation and decomposi-

## 100 SULPHURIC ACID CONCENTRATION

tion arising from the acid being concentrated in the pots. In designing these towers, the probable temperature of the exit gases was carefully considered. It was realised that dilution rather than heating of the feed acid would occur if too much cooling of the exit gases was effected. The towers were lined with Obsidianite bricks and packed with Arklow quartz.

The Dreyfus pots were of the standard design (3 ft. 4½ ins deep by about 3 ft 6½ ins. mean diameter) except that at the acid level a special cast-iron shield was provided, to reduce corrosion of the pot at this point. The pots were ~~rested~~ <sup>supported</sup> on four ~~cushion~~ <sup>curbstone</sup> blocks, and were coke fired, the products of combustion passing through a semi-circular arch under the pot, and around "wheel" flues, being finally discharged to a chimney-stack. Two stacks, each 32 ft. high by 2 ft square, were provided for the four pots. The hot concentrated acid overflowed from the pot into a cast-iron cooling-collecting vessel, from which it was led through a trough to a cast-iron egg. From here the acid was blown to an elevated wrought-iron storage boiler arranged so that tank barges or railway tank wagons could be filled at will

The vapours leaving the recuperator towers were passed through a water-sprayed lead box to a coke scrubber, arranged to afford a downward flow of the vapours and condensate.

A suction equivalent to about ½ in. of water was

maintained at the Dreyfus pots by the operation of a Kestner high-pressure regulus metal fan.

The plant as described worked continuously for about twelve months, during which time several weak points were disclosed.

Difficulty was experienced in maintaining the cover of the pots gas-tight, and in spite of the shield previously referred to, appreciable corrosion of the pots took place at the acid line. These difficulties were overcome by modifying the design of the Dreyfus pot and its accessories in the manner indicated in Fig. 23.

Escape of acid fumes at the dish of the recuperator tower was effectually prevented by the provision of a cast-iron cover, the point between the tower and the cover being rendered gas-tight by packing with asbestos and silicate of soda.

The lead fume-collecting box was a point at which much wear and tear was experienced, but this was considerably reduced by profuse water cooling.

One of the weakest points of the plant was the inadequate cooling facilities for the concentrated acid. This led to the adoption of a water-sprayed cast-iron cooler, consisting of ten 9 ft. lengths of 4-in. cast-iron pipe arranged in the form of a serpentine.

The modified plant was practically foolproof, and was capable of concentrating 18 tons of

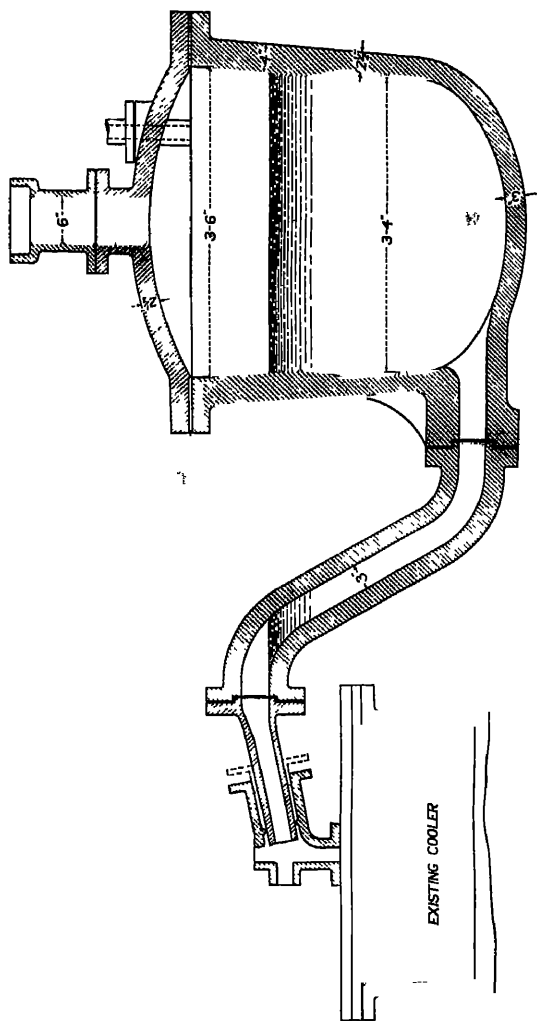


FIG. 23.—DETAILS OF A DRYFUS POT.

sulphuric acid from 93 per cent to 96.5 per cent.  $\text{H}_2\text{SO}_4$  per day.

Control of the plant was effected by maintaining the temperature of the acid at a point approximately 6 ins. from the bottom of the pot at  $315^\circ \text{C}$ ., and by keeping the strength of the condensed acid leaving the coke scrubber below  $148^\circ \text{Tw}$ . If this specific gravity was exceeded, it was evident that dissociation was occurring

The cast-iron pots were cleaned out about every two months, and the coolers every three months. In this connection, a 1-in. everset syphon was provided for withdrawing the acid from the coolers and pots.

During the total working of the plant, 8000 tons of concentrated acid were produced. Twelve pots were used, but four of these were in good condition when the plant was finally shut down. The average coke consumption was 2.4 cwt per ton of 96.5 per cent. acid produced, while the loss of  $\text{H}_2\text{SO}_4$  in concentration was 4.3 per cent

The cast-iron concentrator made by the Buffalo Foundry and Machine Co., of America, possesses many interesting features. This system, which is illustrated in Fig. 24, operates as follows —

The products of combustion from a coke fire are passed around the pot at a temperature of about  $800^\circ \text{C}$ , and thence through a heat interchanger to the recuperator. This latter is a packed tower comprising four cast-iron sections,



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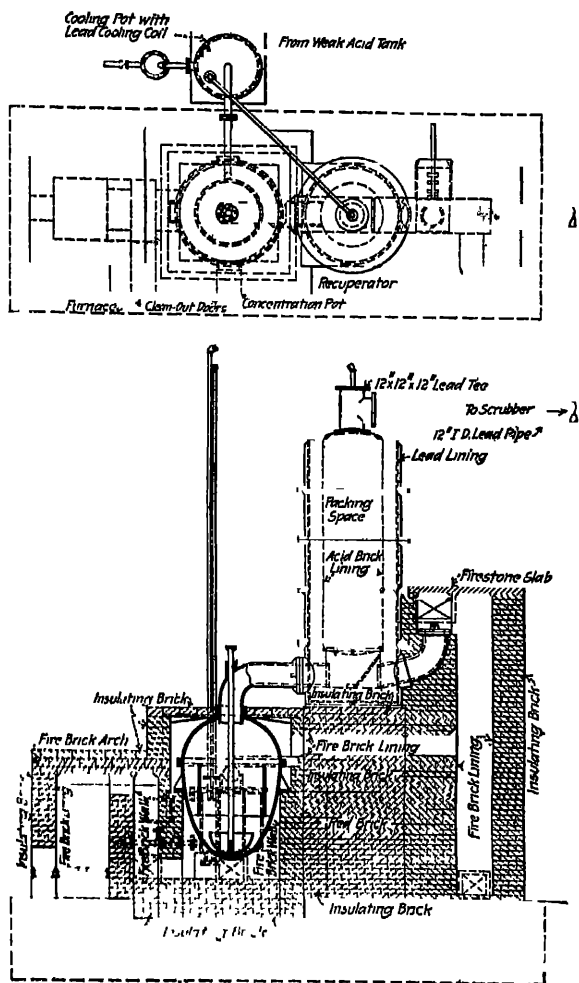


FIG. 24.—BUFFALO TYPE OF CAST-IRON POT CONCENTRATOR.

each 2 ft. 6 ins. by about 4 ft. diameter, lined first with lead, and then with acid-resisting bricks. The furnace gases at a temperature of about 300° C. enter the tower at the same time as the products of dissociation from the pot, and discharge at the top to a 6 ft. by 6 ft. by 3 ft. scrubber. The acid to be concentrated is fed to a heater-cooler, where it is heated by the hot concentrated acid from the pot. From this vessel the acid is elevated to the top of the recuperator, in which it is further heated by the ascending hot gases and vapours. The partially concentrated acid leaving the recuperator flows into the pot where the final concentration takes place. In addition to the bottom firing of the pot, a further supply of heat is provided by hot air from the heat interchanger. This is introduced under pressure near the bottom of the pot, and impinges on a removable liner. A shield of high-silicon iron is provided to protect the pot at the acid line.

It is claimed for this system that there is less dissociation of the acid into  $\text{H}_2\text{O}$  and  $\text{SO}_3$  than is usual in direct-heated concentrators of this type. About  $1\frac{1}{2}$  to 2 cwt of coke are used per ton of acid produced, but this depends on the strength of feed acid and the degree of concentration.

## CHAPTER VIII

### MISCELLANEOUS PROCESSES

#### CONCENTRATION IN HEATED TUBES

ONE of the earliest of the systems employing pipes or tubes for the concentration of sulphuric acid was that of C Krell (B P 1827, 1894).

Krell's apparatus consists of a cast-iron tube about 9 ins. diameter by 8 ft long, arranged horizontally in a bath of molten lead. The lead bath is a cast-iron vessel, 6 ft. 6 ins. long by 1 ft. 6 ins. wide by 2 ft. deep, set in brickwork over a coal fire. A tight joint between the jacket and the protruding ends of the tube is secured by water cooling, thus maintaining the lead in the solid state at this point.

In a later patent of Krell's (B P. 5063, 1906), pipes for the concentration of sulphuric acid are described, having an outer shell of ordinary cast iron, with a lining of chilled white cast iron.

A modification of this system is employed by Strzoda (B.P 26732, 1913), in which the lead bath is dispensed with, the tubes being set directly over a furnace. A description of this type of concentrator is given in the *Z. angew. Chem.* of 1918.<sup>1</sup> The tubes are made of ferrosilicon alloy surrounded by a jacket of cast iron, the annular space being filled with an acid-proof cement as a further protection of the cast iron. A series of tubes is arranged on the bed of a furnace in such a manner that the acid gravitates from the first

<sup>1</sup> *J S.C.I.*, 1918, 688A.

tube to the last, and finally to the cooler and receiver. The vapours are taken from each connecting bend to a condenser consisting of water-cooled lead pipes.

In place of the condenser, Petersen employs a small recuperator tower, in which 50 per cent. acid is converted to acid of about 90 per cent. strength by dissolution of the  $\text{SO}_3$  evolved in the tubes. The acid leaving the recuperator is fed to the concentrator, where a strength of 97–98 per cent. is reached.

Krell-Strzoda plants with Petersen towers have been installed at several works, with very satisfactory results. Although the fuel consumption is high—about  $3\frac{1}{2}$  cwt. per ton of 94 per cent.  $\text{H}_2\text{SO}_4$ —this is counterbalanced by the high concentration efficiency, only 1 per cent. of very weak acid ( $1.5^\circ \text{Tw.}$ ) being produced when concentrating to 94 per cent.  $\text{H}_2\text{SO}_4$ . The number of tubes employed depends upon the output required, about 0.9 ton of 97 per cent.  $\text{H}_2\text{SO}_4$  being produced per tube per twenty-four hours. It is important that the tubes should be kept free from “sludge.” If cleaning is neglected, and crusts are allowed to develop, the tubes will be burned, and thus rendered useless.

CONCENTRATION UNDER REDUCED PRESSURE IN  
LEAD VESSELS

Several processes have been devised with the object of lowering the temperature of concentration, so as to make it possible to produce acid of comparatively high strength in lead vessels. In these systems concentration is carried out under reduced pressure, and thus complications are introduced into the design of the apparatus. Many of these processes are rendered impracticable by reason of such complications.

One of the more successful systems is that of Krell (B.P. 363604). The essential features of this apparatus are illustrated diagrammatically in Fig. 25. The acid is concentrated by passing through a tube, A, heated in an oil-bath, B. The tube is stiffened against the effect of the partial vacuum maintained therein by the provision of perforated plates, C. The holes in these plates are so arranged that the acid is made to proceed in a zig-zag manner. The plates, D, divide the vapour space into three separate compartments, connected through the pipes G, G<sub>1</sub>, G<sub>2</sub>, and the coolers F, F<sub>1</sub>, and F<sub>2</sub>, with the vacuum pipe, V. In this way, weak acid is condensed by F, while comparatively strong acid is obtained from F<sub>2</sub>. The weak acid is fed to the tube from the tank, T, through the jacket of the acid cooler, H, thus utilising the heat of the concentrated acid leaving

the tube by the pipe I. The cooler, which terminates in the receiver, K, must be of such a length that the acid can descend against the

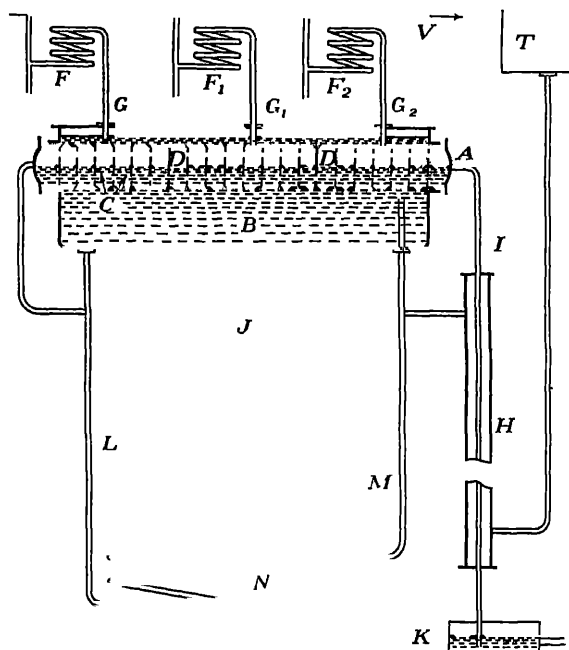


FIG. 25.—KRELL'S VACUUM CONCENTRATOR.

partial vacuum under which the plant is operated. The temperature of the oil-bath is maintained by heating the coil, N, in a furnace, thus producing a constant circulation of hot oil through the pipes L and M.

J. Patten<sup>1</sup> concentrates weak sulphuric acid by passing it through a series of lead chambers, in which it is heated by means of steam coils. The chambers are maintained under reduced pressure, so that the operation can be carried out at comparatively low temperatures. Constructional details of the apparatus are given in U.S P.'s 1286080 and 1286188, of 1919.

The Badische Anilin und Soda Fabrik<sup>2</sup> (G.P. 302553, 1917) employ tubes of iron homogeneously covered with lead, to resist the effect of partial vacuum.

#### ~~ELECTRICALLY~~ HEATED FUSED SILICA STILL

Some interesting results obtained with a small electrically heated silica still were reported by Prof. J. C. Olsen, of Brooklyn Polytechnic, to a meeting of the American Institute of Chemical Engineers, at Denver this year.

It appears that the still in question, designed and constructed by S. L. Tyler, of the Thermal Syndicate, Ltd., was made exclusively of Vitreosil, including the condenser, and inasmuch as the heating element was also enclosed in a Vitreosil tube, the apparatus was peculiarly adapted for sulphuric acid concentration. It is composed of three units, connected in such a way that the acid fed into the first unit overflows into the second, and thence into the third, from which the final

<sup>1</sup> *J.S.C.I.*, 1919, 718A.

<sup>2</sup> *Ibid.*, 1921, 388A.

excess drips Three units may be worked continuously. Any impurities which accumulate in the still can be removed in the drip from the third unit.

The contribution of Olsen describes a number of tests, to ascertain the thermal efficiency and capacity of the still. It was demonstrated that the electrical energy could be utilised with an efficiency as high as 92 per cent. The purity of the resulting acid was of a high order, and the output in the case of sulphuric acid was 145 lb. per twenty-four hours. Sulphuric acid can be concentrated in such a still to more than 97 per cent.



## CHAPTER IX

### TRANSPORT AND STORAGE OF CONCENTRATED SULPHURIC ACID

A CONSIDERATION of peculiar importance, after chamber acid has been concentrated to the required strength, is the method of storage and transport. Questions on this subject are often asked, not alone by users of sulphuric acid, but also by manufacturers

It will be appreciated that no hard and fast rules can be laid down. From the point of view of transport, everything depends on the quantity of acid required and the place to which it has to be delivered. If the customer has a railway siding into his works, then it is usual to recommend the installation of wrought-steel boilers for the storage of C.O.V., 94–96 per cent.  $\text{H}_2\text{SO}_4$ , or lead-lined tanks for the storage of B.O.V. At a number of works wrought-steel boilers have been used for the last-named strength of acid with satisfactory results.

If the factory to which the acid is to be delivered is not provided with railway facilities, and has no storage tank, then it is usual to deliver in drums or carboys, dependent on the requirements of the client in the matter of strength and colour of the acid required. Drums are specially adapted for C.O.V., although they can be used with advantage for B.O.V. In some cases, where colour and purity are essential considerations, it will be necessary to deliver in carboys.

Where the acid is needed for export, it is

important to ensure that the packages are especially suitable, so that they arrive in sound condition and order. In view of the destructive character of sulphuric acid, it is equally important to ensure that in the event of an accident arising in the handling of the package, the contents do not cause any external damage, otherwise claims may be lodged by the shippers or shipowners.

It is proposed to deal with the various modes of transport, and as the authors have found that the exact regulations applying to the transport of acid under varying conditions do not appear hitherto to have been collated, an attempt will be made to fill a long-felt want in this connection.

#### THE TRANSPORT OF SULPHURIC ACID BY RAIL

According to the Special Classification of Dangerous Goods by Merchandise Trains, issued by the Railway Clearing House, concentrated sulphuric acid will be accepted for rail transport in the following forms of packing :—

“(1) In securely closed, well-luted and tied-over earthenware or stoneware jars or stoneware bottles, enclosed in wickerwork, or packed in sawdust, straw, wood-wool, or whiting in cases which must not contain other chemicals by which contact with sulphuric acid might cause fire or explosion

“(2) In securely closed, well-luted and tied-over bottles, packed as above

(3) In carboys.

(4) In 10-gallon steel barrels

(5) In approved steel drums. The gross weight per drum not to exceed 1400 lb. The drums not to be accepted unless in good condition, and free from rust.

(6) In loose tanks in company's wagons.

(7) In loose tanks in owner's wagons.

(8) In owner's tank wagons "

The method of packing described under Nos. 1 and 2 in the above conditions (*i.e.* stoneware or glass bottles in cases) is generally employed only for the transport of small quantities of pure acid. For traffic in ordinary "oil of vitriol," the less costly containers enumerated from (3) to (8) are used.

### CARBOYS

The following regulations as to traffic in carboys were issued by the British railway companies in 1920.—

"(1) *Definition of term 'carboy'*. The term 'carboy' means a globular bottle of not more than twelve gallons capacity,\* made of glass not less than about one-eighth inch thick, in any part, practically free from striae and bubbles, carefully annealed, and with the initials of the maker or other distinguishing mark, on the neck.

*\* (For liquids not exceeding 1.2 specific gravity, carboys up to fourteen gallons capacity may be used).*

(2) *Straw packing*.—Each carboy must be firmly packed in a hamper of iron or wickerwork, with a minimum thickness of half an inch of straw between the hamper and the carboy. This packing must be renewed as soon as it loses its elasticity, and the hamper must be kept in good repair. The straw packing in the carboy hampers, when handed to the Railway Company, must be sufficiently damp to prevent fire.

(3) *Stoppering and luting*.—Each carboy must be provided with a good earthenware or glass stopper\* and must either be (a) well luted with plastic (moist) clay, or (b) well luted first with plaster of Paris and then a layer of moist clay placed over the plaster of Paris, the stopper in all cases to be tied over with a waterproof material to keep the clay moist, and then with strong canvas, firmly tied or wired round the neck of the carboy. Other equally effective means of luting may be used, provided the stopper is in all cases firmly secured and luted, so that the acid cannot escape. An effective method of securing the stopper is by means of a flat metal band, passing round the neck of the carboy and over the canvas (see Fig. 26).

*In the case of certain specified chemicals, an effective vent in the stopper is necessary.*

\* Carboys containing hydrochloric acid—muriatic acid or spirit of salt—may be stoppered with cork bungs luted with paraffin wax covered with canvas, the whole to be secured with copper

*wire, or by a flat metal band passing round the neck of the carboy and over the canvas (Fig. 26). When passing in full truck-loads, the carboys may be stoppered with tightly twisted straw stoppers.*

(4) *Loading*.—For traffic in full-truck SINGLE-TIER loads, the carboys must be placed close up to the end and side of the wagon, and fastened together at all points of contact with strong cord or wire (to be provided by the sender), any space must either be battened off with substantial timber, positioned close to the shoulders of the carboy, or filled with other approved packing, such as straw, sacks of straw, <sup>54</sup>old hampers, etc., or alternatively a framework approved by the company may be fitted in the truck to support each carboy separately. The packing material or framework to be provided by the sender. In the case of DOUBLE-TIER loads, each carboy must be placed on a nest of straw between the shoulders of the bottom tier carboys, the two rows of three at either end to be fastened together with strong cord or wire at each point of contact. The carboy hampers must be interlaced with rope, the ends of which must be braced to give firmness, and secured to the buffers or sheet hooks of the wagon.

*NOTE* —The Great Western Company do not carry nitric or sulphuric acids in double-tier loads, and require the end hampers in single-

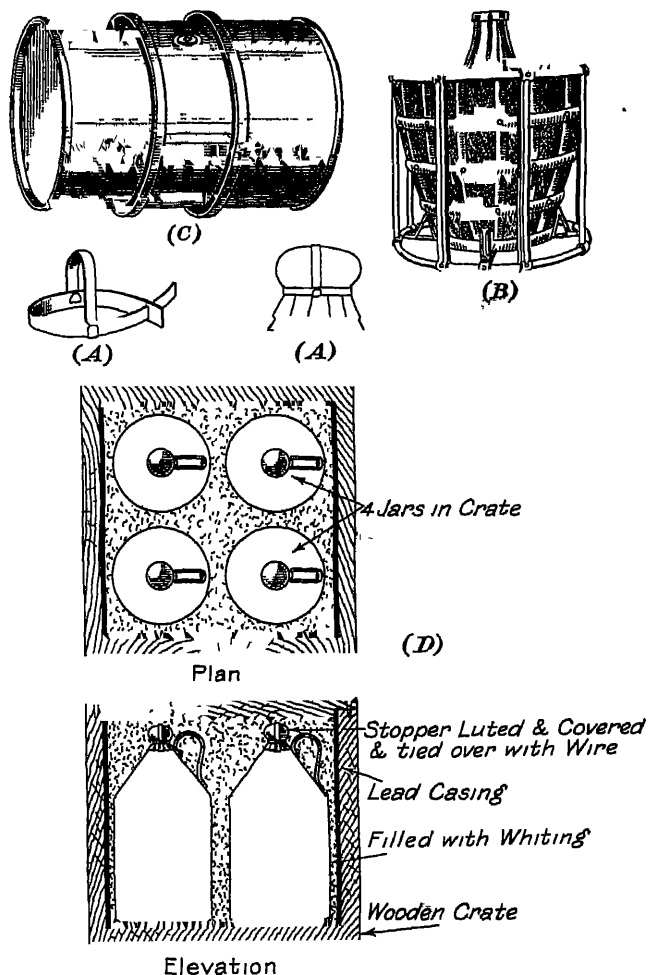


FIG. 26.—AA, STRAP AND COVER; B, CARBOY HAMPER (SAFETY TYPE); C, STEEL ACID DRUM; D, PACKING-CASE WITH EARTHENWARE JARS.

*tier loads to be secured to the ends of the truck with strong cord fastened to the buffers or sheet hooks.*

In the case of single carboys or part loads, the carboys and hampers must be packed in substantial flat-bottomed wooden boxes, crates, or tubs. Carboys in boxes, crates, or tubs must not be loaded on the top of other goods, nor other goods loaded on the top of such carboys. Goods liable to be damaged in the event of breakage or leakage of the contents of the carboys must not be loaded near them."

The standard capacity of carboys of British and American manufacture is 10 gallons; carboys of continental origin usually contain about 13 gallons (60 litres).

Stoppers are made of glazed stoneware or brick, and are usually luted with plaster of Paris before being covered with moist clay and finally tied over with canvas.

Wickerwork baskets, formerly used for the conveyance of carboys, have been superseded almost entirely by the more satisfactory fluted hoop-iron hampers originated by R. Leigh (B.P. 3991, 1876). These hampers are both rigid and light, and will give comparatively long service if occasionally given a protective covering by dipping in black varnish made of hot pitch and creosote oil.

The minimum thickness of straw packing allowed

by the British railways is half an inch, but at least one and a half inches are required to ensure adequate protection.

The necessity for boxes or crates for single carboys may be overcome by the use of the "safety" crate illustrated in Fig. 26 (H. Leigh, B.P. 158028, 1921). This is an outer frame of fluted hoop iron, and is made to receive a 10-gallon carboy hamper. Owing to the base being of the same diameter as the top, this crate is not liable to overturn in a railway truck; it is therefore approved by the Railway Clearing House for the transport of single carboys or small lots.

#### STEEL DRUMS

The following specification of steel drums for the conveyance of sulphuric acid was issued by the Railway Clearing House in 1920.—

"(1) The drums must be made of best quality mild steel sheets.

(2) All joints must be welded

(3) Thickness of metal must be not less than 12 B.G. (2.517 mm.) for body and 10 B.G. (3.175 mm.) for ends.

(4) The ends must be flanged, let into the body of the drum from one to one and a half inches, and strengthened by welded steel hoops either securely shrunk on to the body of the drum with projecting beads to cover the ends, or welded to the body of the drum.



(5) Two solid rolling hoops must be shrunk on to the body of each drum.

(6) Each drum must be provided with a well-fitting screwed steel plug and steel boss, the boss to be welded to the body of the drum. The plug, when screwed home, must not project beyond the rolling hoops or chime.

(7) Each drum must be tested under internal pressure of 20 lb. per sq. in., and proved air-tight, and this test must be repeated whenever the drum shows signs of deterioration, and at intervals of not more than six months.

(8) The outside of each drum must be painted or varnished, and the paint or varnish must be renewed as often as is necessary to preserve the drum from rusting.

(9) When filling the drums, an air-space of 5 per cent. must be left.

(10) The gross weight of filled drums must not exceed 1400 lb. per drum.

(11) Empty drums must be securely closed air-tight before being returned."

Steel drums for sulphuric acid (see Fig. 26) are made in various sizes, those most commonly used being about 2 ft. diameter by 3 ft. in length, and containing approximately 1000 lb. of C.O.V.

In addition to the screwed plug in the body of the drum, it is usual to provide a similar but smaller plug in the end of the drum at a point near the

periphery and opposite to the central plug. This is used as a means of venting the drum when emptying, thus ensuring a steady discharge of the acid.

It is important that the drums should be drained thoroughly, then tightly closed so as to exclude atmospheric moisture. Alternatively, they may be washed out with water, sufficient to remove all traces of acid, and completely drained.

Not infrequently, small leaks appear at the seams, or round the plug, when the drum is otherwise in good condition. Such leaks can be repaired efficiently by oxy-acetylene welding. Care must be taken, however, to remove all traces of acid before commencing any repair by welding, as explosions of no little violence have been known to occur through neglect of this precaution.

An examination of a number of drums which had been used for the conveyance of sulphuric acid revealed the presence of several lumps of moist white material, in addition to a white excrecence over the inside of the drum. An analysis of this substance showed that it contained .—

11.78	per cent	$\text{FeSO}_4$
18.08	„	$\text{Fe}_2(\text{SO}_4)_3$
25.43	„	$\text{H}_2\text{SO}_4$

The quantity of sulphuric acid present by reason of occlusion in these deposits was much larger than would be caused by the mere surface wetting of a clean drum. It was found, however, that

thorough water-washing was quite effective in removing all traces of acid.

### TANK WAGONS

For the conveyance of large quantities of sulphuric acid by rail, tank wagons are generally employed.

This method is alike convenient and economical, as, apart from the important considerations of freight and other charges, the tanks can be filled and emptied easily and quickly with a minimum of labour.

A modern cylindrical tank wagon is illustrated in Fig. 27. The principal dimensions of such a tank as supplied by Charles Roberts and Co, Ltd., of Horbury Junction, near Wakefield, are as follows :—

Length of tank inside . . . . .	15 ft. 3 ins
Diameter of tank inside . . . . .	4 ft 3 ins.
Capacity, 1,300 galls. . . . .	(About 10½ tons C.O V.)
Length over headstocks . . . . .	15 ft. 4 ins.
Length over buffers . . . . .	18 ft 4 ins
Extreme height over all above rails . . . . .	10 ft. 1 in.

The tank is usually built of three mild steel plates,  $\frac{3}{8}$  in thick, with self-flanged ends of  $\frac{1}{2}$ -in steel plate, the plates being single riveted with  $\frac{3}{4}$ -in. rivets at  $1\frac{1}{4}$ -in. centres, and caulked thoroughly both inside and outside to prevent leakage. The manhole is formed by a cast-iron block riveted to the top of the tank and covered by a lid of mild steel. A tight joint between the manhole and the

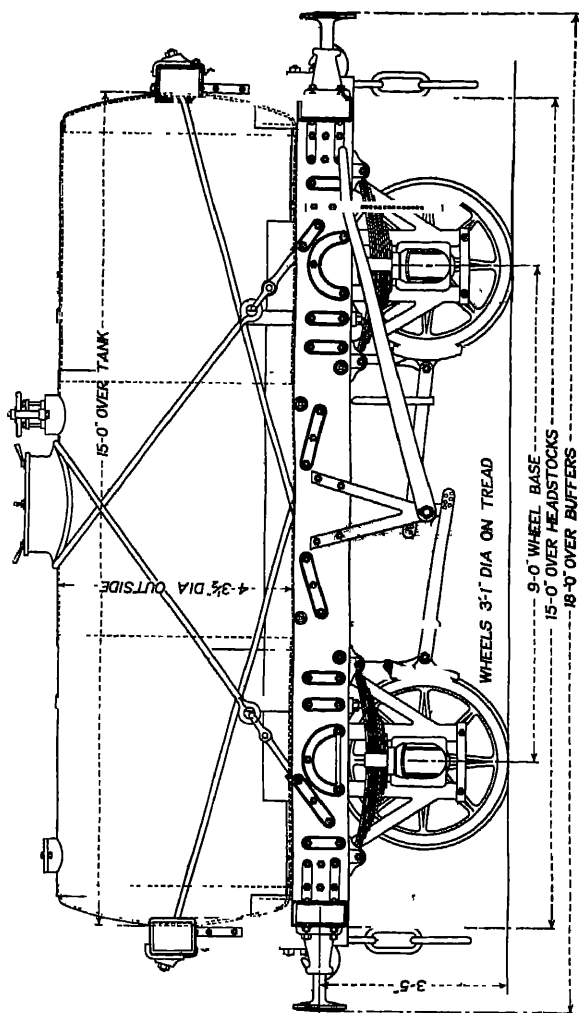


FIG. 27.—RAILWAY TANK WAGON.

cover is made with a rubber ring, which should be of 1-in. section round rubber.

The arrangement for discharging the tank is a cast-iron double arm outlet, bolted to a cast-iron block on the bottom of the tank, and provided at each end with 2-in. cocks.

Cast-iron plug cocks are usually fitted by the makers of the tank, although these are by no means the best type for the purpose. Solid-bottomed gland cocks are certainly more satisfactory from the point of view of leakage, but these are very liable to "seize," especially in cold weather, when attempts to open them generally result in a fractured plug. Regulus metal cocks with "Ironac" plugs are sometimes provided, but these suffer even more than cast iron from the aforementioned defect. On the whole, gun-metal gland cocks with solid bodies are to be preferred, as although they are more expensive initially, they are certainly more economical and efficient in operation than either regulus metal or cast iron.

As an additional security, an internal plug valve having a regulus metal plug on a cast-iron seat is fitted immediately above the outlet. This may either be direct acting, or may work through a lever, both types being operated from the top of the tank by a cast-iron hand-wheel. In the case of the direct-acting type a clockwise movement of the wheel lowers the plug on to its seat, while

in the lever type the same rotation of the wheel opens the valve by raising the plug. Apart from the confusion which often occurs as a result of this dissimilarity, there is much to recommend the adoption of the direct-acting valve as a standard fitting. When an internal lever is used, wearing surfaces are introduced, which are often a source of trouble and expense.

At one end, and on the top of the tank, a cast-iron syphon block is usually provided. This is used either as a means of connecting an air-pressure pipe or as a point from which the tank may be emptied by syphoning or pumping. During transit this is closed by means of a blank flange.

The tank is carried on pitch-pine bearers, and is secured to a timber underframe by two iron straps and two iron rods. The latter, which pass round the manhole casting, are fitted with shackles and adjusting screws for tightening. Steel frames are seldom used for acid tank wagons. Although they are mechanically stronger, and under ordinary conditions more durable, they are more liable to damage by corrosion than are the timber frames usually provided.

The underworks of the wagon are of standard type, made to conform to the Railway Clearing House specification. Axle boxes are now fitted for oil lubrication, these being much more satisfactory than the grease boxes hitherto used. The importance of thorough lubrication of the journals

cannot be unduly stressed, as neglect in this respect results in "hot bearings," with consequent coring of the metal and involving expensive repairs.

On each side of the wagon is fitted a double brake, operated by a long hand-lever. The brake push-rods are usually situated directly below the tank outlet cock, a position in which they are extremely liable to corrosion by spilled acid. Special precautions are necessary, therefore, to protect these rods, either by the provision of a drip-tray under the cock, or by covering the rods with a special paint or varnish. When replacements are necessary it is advisable to use heavier gauge metal than that of which the rods were originally made.

The running costs and ultimate life of a tank wagon are affected by three factors: (a) treatment at works; (b) treatment by railway companies; and (c) maintenance. These will be dealt with briefly *seriatim*.

In order to prevent corrosion on the outside of the wagon, reasonable care must be exercised in the filling and emptying operations, and any unavoidable spillage of acid should be removed immediately by water washing. When empty, the tank should be securely closed so as to prevent the access of atmospheric moisture, otherwise dilution of the small quantity of acid remaining in the tank will occur to such an extent as to cause serious corrosion.

Tank wagons are often subjected to very careless

treatment by the railway companies. It is not uncommon to find buffers, tie-rods, axle boxes, etc., broken as a result of rough shunting. Wherever there is evidence of such damage, it is advisable to call in at once an examiner of the railway company concerned. In many cases it will be found that the railway company will admit liability and agree to accept an account to cover the expense involved in placing the tank wagon in order. Occasionally the officials of the railway company will attempt to evade liability. It is in these cases that firmness is necessary, and it serves a useful purpose if a log is kept recording the condition of the tank from month to month, and the necessary repairs and overhaul which are made from time to time. Well-kept records cannot lightly be ignored, but personal impressions or assurances frequently are

Periodic and systematic overhauls are necessary if a tank wagon is to be kept in sound running order and condition. If facilities for this do not exist at the factory, then a contract should be made with an outside firm of repairers, many of whom will, for a comparatively small amount, undertake to maintain the tank in good condition and repair. If the work is done at the factory, then it is advisable always to keep a stock of spare parts, such as plug valves and cocks, manhole covers and axle boxes, etc., so that repairs may be executed with as little delay as possible.



Attention should be directed to the wearing of the wheels of acid tank wagons. The extent to which wear takes place is a function of the character of the permanent way on which they run. Obviously, if tanks have to travel over many curves, the wear will be appreciably greater than on straight tracks. Experience indicates that an acid tank wagon will run for eight years prior to the wheels needing to be turned. It is a wise procedure to gauge the wheels periodically.

Tank wagons must be fully loaded (subject to the allowance for possible expansion), unless fitted with wash plates approved by the Railway Clearing House. They may then be used for variable loads from half to full.

Tank wagons are subject to rigid examination by railway authorities, and are not accepted for conveyance, either full or empty, unless in good condition and securely closed.

#### THE TRANSPORT OF SULPHURIC ACID BY ROAD

The use of carboys or steel drums for the conveyance of sulphuric acid is not to be recommended except for very small quantities. A much more satisfactory method, and one which is fast becoming general practice for road transport, is the use of a steel tank carried on a motor wagon.

A cylindrical tank is employed for this purpose, similar in construction to the railway tank already described, but of smaller dimensions, holding from 2 to 5 tons.

If the tank is to be in constant use, it may be fixed permanently to the motor wagon, which may also carry a small motor-driven air compressor for the discharge of the acid. When the deliveries of acid are not sufficiently frequent to warrant the whole-time employment of a motor wagon for this purpose, a loose tank may be used, this being mounted in such a manner that it can readily be placed on the wagon when required.

Fig. 28 illustrates an arrangement by which two cylindrical tanks may be lifted from or lowered to a motor wagon, as well as supported when not in use. Each tank is mounted on pitch-pine bearers, and secured to the frame by means of chains which pass round the manhole casting. The solebars are provided with four hooks as a means of attaching the sling chains. These chains are secured in pairs to slow thread screws, operated by means of a capstan.

It is necessary to raise the tank only a few inches from the wagon, so that the operation of loading or unloading can be performed in a minimum of time.

In the North of England and the Midlands it has been the practice for more than thirty years to use tanks 8 ft. long by 2 ft. 9 ins. diameter, made of mild steel riveted plate  $\frac{3}{16}$  in. thick, throughout, with a filling funnel in the centre of the tank, forming a suitable manhole. Such tanks are provided with a bottom outlet cock, to which a double-flanged wrought-iron bend,  $1\frac{1}{2}$  ins in

diameter, is attached. On the other flange is fixed a  $1\frac{1}{2}$ -in. gunmetal gland cock.

The tanks are carried on cradles fixed to two pitch-pine runners, which constitute part of a suitable four-wheeled carriage, or chassis, to which a pair of shafts is attached, so as to admit of the tank wagon being drawn by horses, two of which

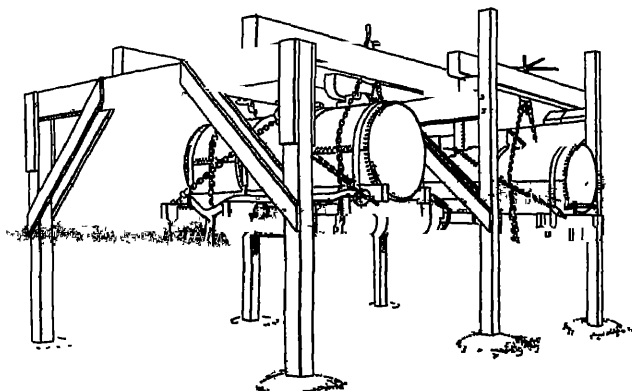


FIG. 28.—LOOSE ACID TANKS.

are invariably employed. The tare weight of the tank and chassis is usually about 25 cwt., and approximately 45 cwt. of B.O.V. are conveyed in such road tank wagons. It is usual for the latter to discharge into lead-lined cisterns at the various mills and factories to which the acid is delivered. The customary size of the storage cisterns is 6 ft. 6 ins. by 3 ft. 6 ins. by 2 ft. 6 ins. deep. These storage tanks each hold about 52 cwt. of acid,

and are protected against rain by a suitable double-pitched cover in wood, which is felted and tarred.

An important factor affecting the life of these acid tank wagons, as indeed any kind of wagon or package made of steel, is that the temperature of the acid at the time of loading should not exceed  $20^{\circ}\text{C}$ . Some years ago one of the authors had occasion to make an independent investigation concerning abnormal wear of acid tank wagons, and found that this was almost wholly due to the tanks being loaded with acid having a temperature of  $40\text{--}45^{\circ}\text{C}$ .

#### THE TRANSPORT OF SULPHURIC ACID IN SHIPS

Shipping regulations regarding the conveyance of sulphuric acid vary considerably: many companies will carry corrosive acids only under restrictions.

Generally speaking, however, vitriol will be carried as a deck cargo in drums or carboys, provided that they are stowed so as to be safe and secure, and readily jettisoned in case of danger, and so that neither the stability of the ship nor the free communication of the crew on the deck is dangerously interfered with.

Small consignments may also be carried on deck in securely stoppered glass or stoneware bottles in wooden cases containing two or four such bottles carefully packed in a mixture of soda ash and wood dust, or other suitable material (see Fig. 26).

The maximum weight of any single case should not exceed  $3\frac{3}{4}$  cwt. Some shipping companies will only carry acid in this manner.

Another method which may be used in some cases is to line strong wooden boxes with lead of 5 or 7 lb. strength, leaving a small filling hole on the lead, which is sealed by welding after the boxes have been filled to 92-95 per cent. of their capacity.

Large cargoes of acid are carried under deck in drums, subject to the observance of certain precautions. The following notes regarding this method are taken from a Memorandum relating to the Carriage of Dangerous Goods and Explosives in ships, which is issued by the Board of Trade (1923)

The acid can be carried with safety under deck if a layer of slack coal not less than 1 ft in depth is laid at the bottom of the hold and carefully levelled off. Then a tier of drums should be stowed upon it, and when the first tier is completed additional coal should be added and levelled off. (Slack coal known as "breeze," "smithies," "smalls," or such trade types of coal can be used for this purpose.) A further tier of drums can then be laid, and the process of filling in with the small coal again resorted to, and so on to a height of as many as four tiers.

In the event of leakage, coal, even in a powdered state, will not evolve heat by reason of the presence

of sulphuric acid, and the marketable condition of only so much of the coal as is wetted by the sulphuric acid is affected.

The possible results that may be anticipated as regards spontaneous combustion in a cargo of coal on the surface of which drums of sulphuric acid have been embedded are —

(1) If the sulphuric acid escapes into the coal spontaneous combustion ~~will not take~~ place within the region of the leakage.

(2) If the spontaneous combustion takes place first, then the rupture of the drums, and consequent escape of the sulphuric acid, will retard or extinguish the fire by the production of sulphurous acid vapour, in which combustion cannot be ~~sustained~~. This gas has a pungent odour and a strongly suffocating effect, so that great care should be taken to keep away from it.

Any coal that has been wetted with sulphuric acid should not afterwards be used.

It is the practice at some ports to stow sulphuric acid in a compartment by itself on a layer of chalk, but the leakage of sulphuric acid on to the chalk would produce carbonic acid gas, a heavy, odourless gas which it is dangerous to inhale, and which gives no warning of its presence. For these reasons, the ventilation of a space where this practice is followed should be carefully attended

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to before any person is allowed to enter the compartment, the down cast being carried as low as possible.

It is recommended that wherever sulphuric acid is carried under deck the precautions indicated above should be observed, but it is, of course, to be understood that drums of sulphuric acid should not be stowed on coal known to be specially liable to spontaneous combustion.

### TANK BARGES

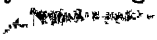
For short journeys by river or canal, barges fitted with tanks may be used for the conveyance of sulphuric acid. In some cases part of the hold of the barge is converted into a tank by lining with lead. A better method, however, is to use cylindrical steel tanks as containers for the acid, two or four such tanks, having a total capacity of about fifty tons, being arranged so that the weight of the cargo is evenly distributed. The tanks are connected together, so that they can be filled or emptied (by blowing or pumping) from one point. In order not to affect the stability of the barge, the tanks should be loaded to about 95 per cent. of their capacity.

### STORAGE

Storage tanks for all strengths of sulphuric acid may be constructed from lead with suitable wood or iron framework. Wooden tanks are also

employed, having an internal covering of bituminous material, or a lining of acid-proof bricks or tiles. Such vessels are generally used, however, only for the storage of chamber acid or B.O.V., or for concentrated acid when contamination by iron is undesirable. For ordinary C.O.V. it is usual to use wrought-steel storage boilers.

These latter may be raised on brick piers to a height sufficient to allow of a gravity flow of the acid to road or rail tanks as well as carboys and drums. It is usual to arrange a manhole and cover to admit of access to the tank for the purpose of periodical cleansing, and to provide, in addition to the outlet cock, an internal plug valve similar to that described under "Railway Tank Wagons."





## CHAPTER X

### POSSIBLE FUTURE DEVELOPMENTS

ONE can scarcely leave the subject of acid concentration without asking the question, "What of the future?"

Progress in the heavy chemical industry has been very rapid during the last decade, particularly so during the war period, when unusual opportunities were afforded for the trial of new ideas, and for the application of modern or improved processes.

Never previously had the country been called upon to meet such a prodigious demand for concentrated sulphuric acid.

This demand was initially met by the erection of various concentrators of the cascade, Kessler, and Gaillard types.

A few months' intensive working confirmed a long-established pre-war experience, namely, that there is a limit to the economic utility of these concentration plants.

The wide difference in the capacities of these units when producing acid of (say) 92 per cent.  $\text{H}_2\text{SO}_4$ , and (say) of 96-98 per cent.  $\text{H}_2\text{SO}_4$ , is striking.

In point of fact, not a few managers and chemical engineers have reached the conclusion that above a concentration of 92 per cent., few concentrators work economically. Their productive capacity is reduced appreciably, and wear and tear are

increased out of all proportion to the value of the higher strength acid yielded.

For certain purposes, such as the sulphonation of organic products, the manufacture of explosives, and other requirements of this order, the use of 96-98 per cent. acid is essential, and has an important influence on the duration of the chemical reactions being effected. This factor, in turn, affects capital expenditure and working costs.

The Ministry of Munitions appreciated this fundamental consideration, and erected plants to produce Oleum.

The demand for Oleum has to a large extent disappeared with the war, and notwithstanding that most of the plants in question have been dismantled during the reconstruction period, a little reflection will make it evident that an efficient type of concentrator, combined with mixing plant, where provision is made for the use of Oleum as a fortifying medium, will undoubtedly constitute a rational means by which the problem of the production of rectified acid of 96-98 per cent. strength could be solved.

What deters manufacturers from adopting such a combination of plant is not any doubt as to its value or utility, but they are averse to being placed in a position which renders them dependent on Oleum manufacturers.

At the present time it can be accepted as axiomatic that the contact process is essentially a

process for the production of high strength acid. Equally, for the production of 70 to 80 per cent. strengths, the chamber process with concentration plants "holds the field."

But when one approaches intermediate strengths, geographical considerations and special circumstances are the deciding factors in determining whether such requirements could be met (*a*) *via* Oleum, (*b*) by the concentration of chamber acid, or (*c*) by mixing weak acid concentrated to an economic strength with Oleum.

The whole aspect would be changed if it were possible to produce simultaneously on one plant chamber acid and Oleum.

*It is in this direction that future development appears to lie.*

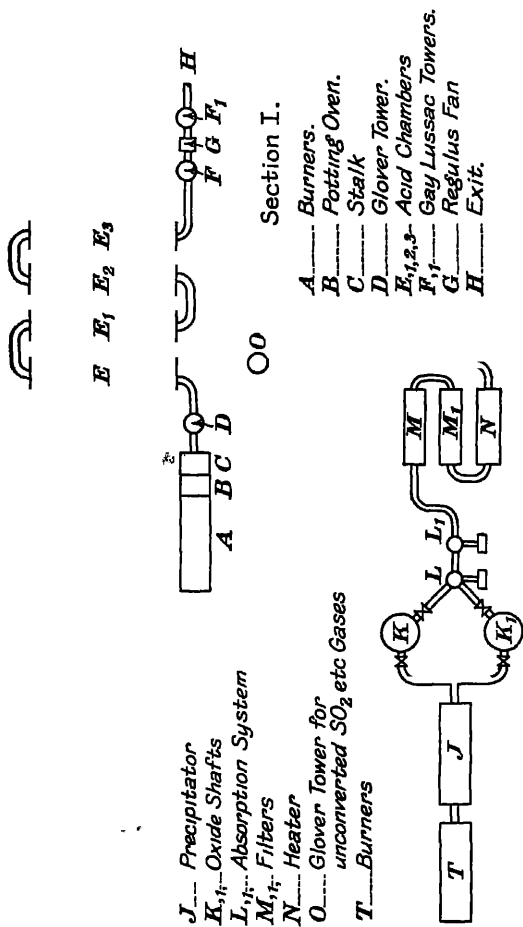
Such a combined plant is much nearer realisation than many are inclined to suppose. Fig. 29 shows diagrammatically two types of plant which should be developed for the specific purpose in question. A few words may be devoted to a consideration of the plants shown.

In the first, two sections of plants are contemplated; one, a chamber plant with its Glover and Gay-Lussac towers, and its complement of chambers. Working in conjunction with this plant is a second one, comprising a burner set, where desiccated air for the combustion of the pyrites, and where the burner gases, after elimination of the dust in a Cottrell precipitator, are led into two oxide

shafts, for conversion of a portion of the sulphur dioxide to sulphur trioxide. The resulting gases emerging from the oxide shafts, which it will be seen can be worked alternately, are led to absorption towers, LL, where the sulphuric anhydride is absorbed in strong acid, and thus C.O.V. of any desired strength can be produced. The unconverted sulphur dioxide is passed through filters and heaters to a small Glover tower fed with nitrous acid. Sulphuric acid is produced as a result of the interaction. Any  $\text{SO}_2$  discharged from the small Glover tower is sent forward to the chamber unit of the system, which is essentially a chamber plant.

The complication of working in conjunction with a complete chamber unit is avoided in the second scheme, which is undoubtedly the one to be preferred. Provision is made here for the unconverted sulphur dioxide leaving the absorbers to pass through bubbling boxes, where they are brought into contact with nitrous acid of a well-defined strength, and where intensive reaction ensues. The Schmiedel system and plant, according to E.P. No. 156328, of 1919, are alike applicable for this purpose.

The crux of the scheme suggested centres around the oxide shaft and the efficiency of the conversion. Further, it is important that the Oleum produced should be of good colour, and free from iron and other impurities.



Section II.

Fig. 29.—COMBINED CHAMBER AND OLEUM PLANT.

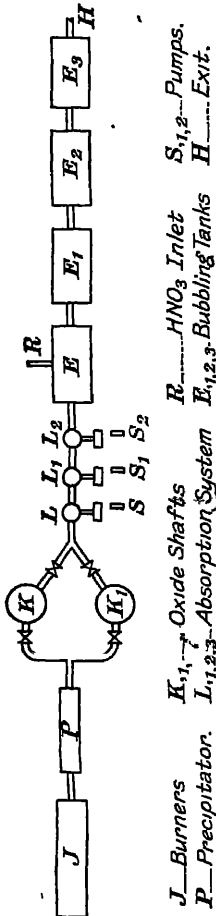


FIG. 29.—COMBINED CHAMBER AND OLEUM PLANT.

The latter condition can be met by the careful operation of a Cottrell precipitation plant for the removal of the oxide of iron dust prior to the gases reaching the converter.

Some research work still remains to be done concerning the kinetics of the oxide shaft. It is known that certain optimum temperature conditions are necessary for ensuring maximum and constant conversion, that the oxide should be in lumps of a specific size, having a given porosity, and that the converter should be discharged of some of the "fines" when a certain resistance is exceeded, but further work is needed. More than all, the economics of the oxide shaft as contrasted with the use of cheaper catalytic bodies than metallic platinum need to be set out.

Silver vanadate may well prove to be an efficient and economic catalyst, when used in conjunction with the second type of plant illustrated in Fig. 29.

Finally, a chapter of this character would be incomplete without affording some idea of the type of plant which is required for producing large quantities of high strength acid from Oleum and sulphuric acid derived from a chamber plant.

Fig. 30 illustrates a suitable arrangement, which consists of a cylindrical apparatus, lined with earthenware, in which the Oleum and sulphuric acid are brought into contact without sulphuric anhydride being evolved. The mixed acids from this vessel first fill completely a special iron ser-

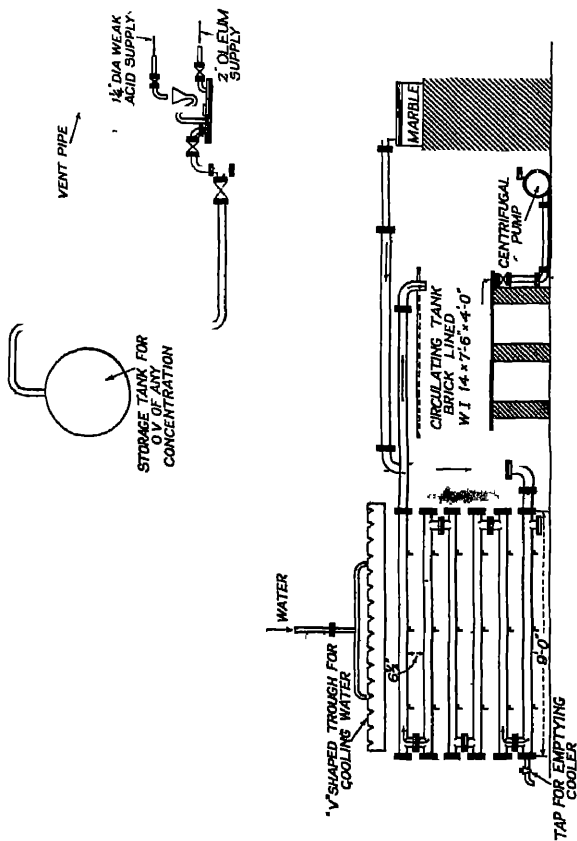


FIG. 30.—OLEUM-ACID MIXING PLANT.



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pentine cooler, which is profusely water-sprayed before being discharged to an enclosed steel tank, lined with acid-proof bricks, where the partially cooled mixed acids are received, and from which tank they are pumped to the cylindrical mixer several times, in order to ensure uniformity of strength and complete cooling. Afterwards, the mixed acid can be pumped to a storage boiler, as shown.

Where smaller quantities of Oleum and sulphuric acid need to be mixed, less elaborate plant can be adopted; indeed, it is possible to run a small feed of Oleum along with (say) 90 per cent. C.O.V. discharged from a cascade, Kessler, or Gaillard concentrator, and to send the mixed acids through a serpentine cooler which is adequately water-cooled, and to discharge the mixed acid of any desired strength into the usual storage tank of the concentration plant.

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